THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

CONDUCTED BY

SIR ROBERT KANE, LL.D. F.R.S. M.R.I.A. F.C.S.

SIR WILLIAM THOMSON, Knt. LL.D. F.R.S. &c.

AND

WILLIAM FRANCIS, Ph.D. F.L.S. F.R.A.S. F.C.S.

" Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster vilior quia ex alienis libamus ut apes." Just. Lips. *Polit.* lib. i. cap. 1. Not.

VOL. XX.—FIFTH SERIES.

JULY—DECEMBER 1885.

LONDON:

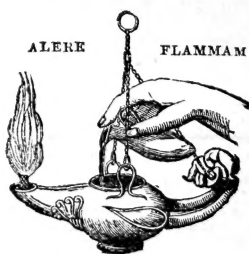### TAYLOR AND FRANCIS, RED LION COURT, FLEET STREET.

SOLD BY LONGMANS, GREEN, AND CO.; KENT AND CO.; SIMPKIN, MARSHALL, AND CO.;
AND WHITTAKER AND CO.;—AND BY ADAM AND CHARLES BLACK, AND
T. AND T. CLARK, EDINBURGH; SMITH AND SON, GLASGOW;—
HODGES, FOSTER, AND CO., DUBLIN;—PUTNAM, NEW YORK;—
VEUVE J. BOYVEAU, PARIS;—AND ASHER AND CO., BERLIN.

"Meditationis est perscrutari occulta ; contemplationis est admirari perspicua . . . . . Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem."—*Hugo de S. Victore.*

—"Cur spirent venti, cur terra dehiscat,
Cur mare turgescat, pelago cur tantus amaror,
Cur caput obscura Phœbus ferrugine condat,
Quid toties diros cogat flagrare cometas,
Quid pariat nubes, veniant cur fulmina cœlo,
Quo micet igne Iris, superos quis conciat orbes
Tam vario motu."

J. B. Pinelli ad Mazonium.

ALERE   FLAMMAM

CONTENTS OF VOL. XX.

(FIFTH SERIES).

NUMBER CXXVI.—NOVEMBER.

NUMBER CXXVII.—DECEMBER.

ERRATUM.

Page 163, line 4 from bottom, *for* ·2478 *read* ·2784.

PLATES.

I. *A Determination of the B.A. Unit in Terms of the Mechanical Equivalent of Heat.* By LAWRENCE B. FLETCHER, Ph.D.*

THE experimental work of the following investigation was completed in 1881, and forms the subject of a thesis submitted to the Johns Hopkins University in that year. In the present paper a more accurate method of calculating the currents from the deflection-curves is used, and some of the other calculations have been revised. The results of the two papers are substantially the same.

The experiment consisted of simultaneous thermal and electrical measurement of the energy expended by a current in a coil of wire immersed in a calorimeter. The result depends upon the values of the mechanical equivalent and the unit of resistance, and gives a determination of either in terms of an assumed value of the other.

The old determinations of Quintus Icilius and Lens have no value, as the resistance is uncertain, as pointed out by Rowland and H. F. Weber.

Joule†, in 1867, made a determination of the mechanical equivalent by this method, assuming the B.A. unit as determined by the Committee in 1863–4 to be equal to 10^9 C.G.S. units. The value of the mechanical equivalent thus obtained is more than 1 per cent. greater than Joule's water-friction

---

* From an advance proof from Silliman's American Journal, communicated by the Author.
† Report of British Association Committee on electrical standards, 1873.
‡ Phil. Mag. S. 5. vol. v. pp. 30, 127, 189.

value. H. F. Weber‡, in 1878, used a similar method, employing the Siemens unit, the value of which he also measured in C.G.S. units. Weber's value of the mechanical equivalent is about one part in two hundred greater than Joule's water-friction value, and one part in four hundred greater than Rowland's water-friction value.

In both Joule's and Weber's experiments a possible source of error seems to have been ignored. The wire was assumed to be at the temperature of the water in which it was immersed, and its resistance was calculated on this assumption. It is evident, however, that the wire was hotter than the water, inasmuch as it was giving heat to the water. The error due to this cause is of uncertain amount. If corrected for this error, the values of the equivalent would be increased and their excess over the water-friction values would become greater than before. To avoid this source of error, the research described below was planned. The suggestion and general plan of the research I owe to Professor Rowland.

The theory of the method is as follows:—A current c, flowing through a wire of resistance R, for a time t, generates an amount of heat represented by $h = \dfrac{c^2 \mathrm{R} t}{\mathrm{J}}$, where J is the mechanical equivalent of heat. The wire being immersed in a calorimeter and put in a circuit with a galvanometer, h, c, and t can be measured. Then if R is measured in B.A. units, the experiment will give a relation between the value of that unit and the mechanical equivalent. In this research R was measured during the actual experiment by connecting its terminals with those of a large resistance R′ and measuring the current c', which flowed through the latter. With this arrangement $c\mathrm{R} = c'\mathrm{R}'$, or $\mathrm{R} = \dfrac{c'}{c}\mathrm{R}'$. Hence $\mathrm{J} = \dfrac{cc'\mathrm{R}'t}{h}$, in which R does not appear, and the uncertainty attaching to its temperature has no effect.

The calorimeter was a cylindrical cup of sheet copper holding about 800 cubic centim. On the bottom of the cup lay a sheet-copper frame which supported three vertical glass rods. Around these the wire R was coiled, forming a helix. The ends of the wire were soldered to stout copper wires, which, insulated by short vulcanite tubes, passed through the wall of the calorimeter and turned down so that they could be placed in mercury-cups. The cover of the calorimeter rested in contact with the water to secure uniformity of temperature. The cover had an expansion-tube and a smaller central tube, which formed one bearing for the stirring-apparatus, another bearing being given by a brass socket on the bottom of the calori-

meter. The stirrer consisted of a spiral blade of sheet copper supported on a brass frame, the upper part of which was tubular, and passed through the central tube of the cover. The stirrer was kept in motion during the experiment by a silk thread, which passed over a vulcanite wheel at the top of the stirrer and ran to a driving-clock. The stirrer formed the escapement of the clock, which ran very uniformly with this arrangement. I estimated the heat generated by the stirrer as two thirds of the whole work of the weights. This is about one thousandth part of the heat generated by the current, and only a rough determination of the correction is needed. The thermometer passed through the tubular upper part of the stirrer, and was clamped to a shelf above in such a manner that its bulb was in the centre of the calorimeter and surrounded by the stirring-blade, which, in turn, was surrounded by the wire which carried the current. The wire was composed of an alloy of platinum and iridium, and was varnished to prevent conduction to the water. Its resistance was about 1·8 ohm. The calorimeter was supported on legs of vulcanite within a copper vessel with double walls, the space between which was filled with water. This water-jacket was provided with a hollow cover, also filled with water, and its inner surface and the outer surface of the calorimeter were nickel-plated and polished. Thus the calorimeter was nearly surrounded by an envelope of fairly constant temperature, the thermometer, stirrer-thread, and connecting wires passing through openings in the jacket.

From the mercury-cups, in which the electrodes of the calorimeter dipped, the wires of the main circuit ran to the battery and galvanometer. These wires were 2·5 millim. in diameter, cotton-covered, carefully paraffined, and twisted together to eliminate direct action on the needle. The battery consisted usually of 24 one-gallon bichromate cells, arranged 4 in series and 6 abreast, and gave a very steady current. In one experiment only 20 cells were used, 4 in series and 5 abreast. The galvanometer-coil for the main current was a single turn of stout wire laid in a groove on a wooden circle of about 80 centim. diameter. A sine-galvanometer was so placed that its needle was in the axis of the single-wire coil and about 1 centim. distant from its plane. This excentricity was rendered necessary by the length of the suspending fibre. The coil of the sine galvanometer was connected with the calorimeter-electrodes by a second circuit, in which a resistance-coil of 30,000 ohms was included. The wires of this circuit were kept apart, as the current was too small to exert an appreciable direct action, and as great irregularity in some

preliminary experiments in which the wires were twisted together was finally traced to leakage, although the wires had a double covering of silk.   Both circuits were provided with commutators.   The sine-galvanometer had a horizontal bar parallel to the axis of the coil.   To one end of this was attached a telescope, beneath which was a short scale which was seen by reflection in the mirror of the needle, and allowed a very accurate setting to be made without bringing the needle to rest.   The needle consisted of two thin strips of steel 1·2 centim. in length, separated by a piece of wood ·6 centim. in thickness.   The circle of the galvanometer was graduated to half-degrees, and read by verniers to one minute.

The needle was acted upon by both currents simultaneously, and by means of the commutators the actions were caused to be in the same and in opposite directions alternately.   The current through the sine-galvanometer is c' in the formula $J = \dfrac{cc'\mathrm{R}'t}{h}$.   The current through the coil on the wooden circle is $c + c'$, and was assumed equal to c, as c' was less than ·00007c. Let G denote the constant of the fixed coil, G′ that of the sine-galvanometer, H the horizontal magnetic force, θ and θ' the deflections when the actions are in the same and in opposite directions respectively.   Then

$$\mathrm{G}c \cos \theta + \mathrm{G}'c' = \mathrm{H} \sin \theta,$$
$$\mathrm{G}c \cos \theta' - \mathrm{G}'c' = \mathrm{H} \sin \theta'.$$

Hence

$$c = \frac{\mathrm{H}}{\mathrm{G}} \tan \tfrac{1}{2}(\theta + \theta'), \quad c' = \frac{\mathrm{H}}{\mathrm{G}'} \frac{\sin \tfrac{1}{2}(\theta - \theta')}{\cos \tfrac{1}{2}(\theta + \theta')}.$$

Let l denote the length of the wire in the fixed coil, and b the distance of the needle from its plane.   Then

$$\mathrm{G} = \frac{4\pi^2}{l\left(1 + \dfrac{6\pi b^2}{l^2}\right)}.$$

Hence the equation for J becomes

$$J = \frac{\left[\mathrm{R}'l\left(1 + \dfrac{6\pi b^2}{l^2}\right)\right]}{4\pi^2 \mathrm{G}'} \frac{\mathrm{H}^2 t}{h} \frac{\tan \tfrac{1}{2}(\theta + \theta') \sin \tfrac{1}{2}(\theta - \theta')}{\cos \tfrac{1}{2}(\theta + \theta')}.$$

I shall discuss in order the quantities contained in this expression.

R′, the resistance of the secondary circuit, is the sum of the resistances of the 30,000-ohm coil, the sine-galvanometer, and

connecting wires. The whole was measured by connecting the terminals of the circuit with a Jenkin-bridge and comparing with other coils, using a high-resistance Thomson-galvanometer. The provisional standard was a 10-ohm coil, A, made by Warden, Muirhead, and Clarke. From this coil the resistance of a 100-ohm standard, B, was obtained by means of a comparator, C, of ten coils, each nearly equal to A, each coil of C being compared with A, and C in series then compared with B. Then A, B, and C were arranged to form a bridge with D, a 1000-ohm standard, whose resistance was thus fixed. E and F, two 1000-ohm coils of a resistance-box, were then compared with D. Finally, a bridge was formed with A, B, D + E + F, and R′, the secondary circuit, giving R′ in terms of A. Elliott's coils were used in making the adjustments, which were always very small, and the temperatures were carefully observed. The result is

$$R′ = 30012\cdot4 \text{ at } 19°\cdot3 \text{ C.}$$

R′ consisted principally of the 30,000-ohm coil, and the variation of this only need be considered. Its temperature varied from 19° to 24° when in use, the mean temperature being 22°·3 C. At this temperature R′ = 30052, which value was used throughout.

The length of the wire in the fixed coil was determined by measuring with a steel tape the distance between two threads fastened on the wire before it was placed on the circle. When the wire was in position, the interval of a few centimetres between the threads was measured. The tape had been compared with standards. Care was taken to avoid difference of tension in the two positions of the wire. The result is

$$l = 264\cdot49 \text{ centim.}$$

The quantity b (the excentricity of the needle) was estimated by holding the tape horizontally over the top of the circle, and reading the positions of the centre of the wire and the galvanometer-fibre. For most experiments $b = 1\cdot2$ centim. It was frequently remeasured, and a correction applied when it varied. The method of measurement is not very accurate; but an error of 10 per cent. in b, which could hardly occur, would only involve an error of 1 part in 3000 in J.

G′ had been determined by Professor Rowland[*] by measurement during the construction of the coil, and also by comparison with another coil. The values are 1832·24 by

---

[*] Silliman's American Journal, 1878.

measurement and 1833·67 by comparison. The mean, giving the second value twice the weight of the first, is 1833·19.

Hence the constant term $= 10996 + 10^7$.

G' has recently been remeasured and found to be 1832·53. My final result is corrected to this value.

H was measured in the following manner :—The circle bearing the fixed coil carried four smaller wires, which could be connected with the battery and an electrodynamometer of the form described in Maxwell's treatise. These four wires with the needle formed a tangent-galvanometer, the other coils being open. Eight pairs of simultaneous readings of the galvanometer and electrodynamometer were taken, comprising all possible combinations of signs of the currents in the galvanometer and the two electrodynamometer-coils. I am greatly indebted to Professor S. H. Freeman, then Fellow of the University, for assistance in these readings.

The expression for H is

$$H = \frac{4\pi^2 nC \sqrt{I}\left(1 - 6\frac{\pi^2 b'^2}{l'^2}\right)}{l'} \frac{\sqrt{\sin \alpha}}{T \tan \phi} ;$$

where C is a function of the dimensions of the electrodynamometer-coils, I the moment of inertia of the suspended coil, n the number of turns of wire in the galvanometer, l' the mean length of one turn, b' the mean distance of their planes from the needle, T the time of vibration of the small coil, α and ϕ the mean deflections of electrodynamometer and galvanometer.

C was known from measurements during the construction of the instrument, and I had been determined by observing times of vibration with and without the addition to the suspended coil of bars of known moment of inertia. These values of C and I had been verified by Dr. E. H. Hall and myself, in connection with a previous research, by comparing the values of H obtained by this method and by the magnetic method, the arrangement of the experiment being such as to make the two results obtain for the same point and time. The value of $C\sqrt{I}$ is 0·18567.

The measurements of l' and b' were made in the same manner as those of l and b.

The results are $l' = 263·91$ centim., $b' = 2·07$ centim., for most experiments. A correction was applied when b' varied. Hence

$$\frac{4\pi^2 nC \sqrt{I}}{l'}\left(1 - 6\frac{\pi^2 b'^2}{l'^2}\right) = ·11069.$$

Each of the angles, α and ϕ, is the mean of eight readings

taken to 1′. The former was about 13°, the latter 6°. T was obtained by observing ten transits with a seconds-clock, allowing the coil to vibrate for several minutes, and then taking ten more transits. The difference between the mean times of the two series divided by the number of vibrations gives T very exactly. The difference between the values before and after the experiment never exceeded 1 part in 3000. The mean value is about 2·42 seconds. H was determined before and after the main experiment.

The quantities in the formula for J remaining to be discussed are t, h, and the deflections. To treat these intelligibly, I proceed to describe the method of experiment exactly.

First, a determination of H was made. The calorimeter was then weighed, filled with distilled water at a temperature usually 2° or 3° below that of the air, carefully wiped with a towel to remove moisture, again weighed and placed in the water-jacket. Its amalgamated electrodes were placed in the mercury-cups with the terminals of the two circuits, the main circuit being broken at the commutator. The water-jacket was kept permanently filled, and stood in a room of fairly constant temperature, so that its temperature changed little during the experiment. The thermometer was placed in position and the stirrer started. During a few minutes readings were taken of the thermometer and of three auxiliary thermometers, giving the temperatures of the jacket, the 30,000-ohm coil, and the air near the stem of the principal thermometer, the time of each reading being noted by a seconds-clock. The circuit was then closed and a galvanometer-reading taken, one of the commutators was reversed and another reading taken, the time of each reading being noted. The time of passage of the mercury of the thermometer over several successive scale-divisions was then taken, also readings of the other thermometers. Two more commutator-reversals and galvanometer-readings followed, then another set of thermometer-readings; and this alternation was continued for about 40 minutes, during which time the thermometer rose about 12° C. Usually sixteen galvanometer-readings were taken and seven groups of thermometer-readings comprising 35 or 40 readings of the principal thermometer. Then the circuit was broken and the calorimeter allowed to cool for two or three hours, during which time groups of readings were taken as before, the stirrer being kept in motion. While this radiation-experiment was in progress another determination of H was made. Finally, the thermometer was removed and the calorimeter taken out and weighed.

The mean of each group of thermometer-readings, corrected for stem error, gives very exactly the temperature of the ther-

mometer for the mean time of that group. The difference between any two of these mean temperatures, corrected for radiation, gives by multiplication into the capacity of the calorimeter and contents the heat generated in the interval. Hence any two groups give a determination of J when combined with the proper values of θ and θ'.

I have combined groups taken 18 to 25 minutes apart, the rise of temperature being 6° to 8°.

In this calculation the differences of temperature of coil, water, and thermometer are assumed to be constant for this interval. The water is cooler than the coil, and the thermometer cooler than the water. Both differences depend upon the rate of generation of heat, and may be put approximately proportional to the square of the current. The rise of the thermometer after breaking the circuit is due to these differences, and was found to be less than 0°·05. The variation of this quantity during the interval in question would be about 3 per cent., as the current changed 1·5 per cent. Hence the variation is 0°·0015; and as the rise of the thermometer is 6° or 8°, the error is negligible.

Two thermometers were used, designated as Baudin 6165, and Baudin 7320. The former is graduated in millimetres, of which about 12 equal 1° C. It had been used by Professor Rowland in his determination of the mechanical equivalent, and compared several times with the air-thermometer. Baudin 7320 is graduated to 0°·1 C., one degree occupying about a centimetre. It had been compared with standard thermometers, its errors plotted, and the error for each degree obtained from the curve. The following tables give the reduction to the absolute scale :—

BAUDIN 6165.			
Reading in mm.	Temperature on absolute scale from 0° C.	Reading in mm.	Temperature on absolute scale from 0° C.
35	0·0	320	24·547
50	1·368	330	25·365
100	5·839	340	26·174
150	10·183	350	26·981
200	14·450	360	27·782
250	18·709	370	28·584
260	19·557	380	29·376
270	20·401	390	30·170
280	21·242	400	30·965
290	22·076	410	31·786
300	22·907	420	32·581
310	23·731		

	BAUDIN 7320.		
Reading.	Temperature on absolute scale from 0° C.	Reading.	Temperature on absolute scale from 0° C.
0	0·122	23	23·108
5	5·092	24	24·122
10	10·110	25	25·137
15	15·090	26	26·152
16	16·093	27	27·166
17	17·094	28	28·179
18	18·091	29	29·192
19	19·086	30	30·205
20	20·081	31	31·217
21	21·085	32	32·230
22	22·095		

The table for 6165 is condensed from Professor Rowland's paper[*] on the mechanical equivalent. Change in the zero point has no effect on the differences of temperature used, but the zero points were determined occasionally in order to get the mean absolute temperature.

The correction for radiation was made in the following manner :—The groups of thermometer-readings taken after breaking the circuit were reduced to mean readings at mean times. Any two of these mean readings gave the radiation for the intervening time. If t' and t'' are the temperatures at the beginning and end of an interval of T minutes, and τ is the mean temperature of the jacket during the interval, then

$$t' - t'' = c\mathrm{T}[\tfrac{1}{2}(t' + t'') - \tau],$$

where c is the coefficient of radiation. In the calculation of c, stem-corrections were applied and a correction made for the heat generated by the stirrer. Hence in the main experiment the temperature-correction for an interval T' is

$$\Delta = c\mathrm{T}'[\tfrac{1}{2}(s' + s'') - \tau'] + \mathrm{K},$$

where s' and s'' are the observed temperatures corrected for stem-error, τ' is the mean temperature of the jacket, and K is the stirrer-correction. The sum of the corrections Δ from the beginning of the experiment added to the stem-corrected observed temperature at any point, gives the temperature which would have been reached in the absence of radiation. The difference between any two of these theoretical temperatures multiplied by the heat-capacity, gives the heat generated in the interval.

[*] Proceedings of American Academy of Arts and Sciences, 1880.

The coefficients of radiation were found to decrease with decreasing difference of temperature between calorimeter and jacket. When this decrease was regular the corresponding value of c was used for each small interval of the main experiment. When the decrease was small and irregular the mean value of c for that day was used throughout. In the revision of the calculations, stem- and stirrer-corrections were neglected in the calculation of both c and Δ, it being obvious that, both being small and quite regular, they are eliminated in this way; and the value of c corresponding to the difference between calorimeter and jacket for each small interval of the main experiment was used in all cases. The mean results of the two methods differ about 1 part in 1000, and the figures in the table of results below are the means of both calculations. The mean values of c for the different experiments vary between $0°\cdot0035$ and $0°\cdot0046$, the general mean being $0°\cdot0040$.

The mean radiation-correction is about 5 per cent., and is the most important source of variable error in the experiment, as the temperature-differences are small, and errors of reading have a large effect. But a 10-per-cent. error in the radiation would only involve an error of 1 part in 200 in J; and as the errors are irregular they are, in a great measure, eliminated from the final result.

The calorimeter was composed of 246 gr. copper, 45 gr. brass, and 6 gr. solder. The specific heat of a mixture of these proportions was measured with Regnault's apparatus. Six determinations gave the value $\cdot0898 \pm \cdot0005$ for the mean specific heat between $24°$ and $100°$. Reduced by Bède's law for copper to the mean temperature of my experiments, it becomes $\cdot0877$. The capacities of the coil and glass rods were calculated from published tables. The whole capacity is as follows :—

Calorimeter . . . . $302\cdot1 \times \cdot0877 = 26\cdot49$
Coil . . . . . . $32\cdot5 \times \cdot0324 = 1\cdot05$
Glass rods . . . . $9\cdot0 \times \cdot177 = 1\cdot59$
Thermometer estimated at . . . . . $1\cdot25$

Total capacity . . . . $30\cdot4$

The values of the deflections were obtained by a graphical method. The galvanometer-readings fell into 4 groups, lying about $26°$ and $3° 45'$ on each side of the zero-point. The readings of each group were plotted separately as functions of the time. From each curve the theoretical mean readings for each interval between two temperatures used in the calcula-

tion of **J** were obtained by measuring a large number of equidistant ordinates, calculating the area of the curve, and dividing by the base-line. If a, b, c, and d are the mean readings thus obtained, $2\theta = a - b$ and $2\theta' = c - d$ as the galvanometer was graduated from 0° to 360°. Thus the zero-point was not used, though observed before and after each experiment.

Below are the results of one experiment in detail. Each value of **J** is calculated from the two temperatures found in the same horizontal line.

<div align="center">

Series of December 9th.
</div>

<div align="right">gr.</div>

Weight of calorimeter and water before experiment .	1157·2
Weight of calorimeter and water after experiment .	1157·0
	1157·1
Weight of calorimeter	343·7
	813·4
Capacity of calorimeter	30·4
	843·8
Capacity reduced to weight in vacuo	844·8
Horizontal magnetic force before experiment . . .	·1960
Horizontal magnetic force after experiment . . .	·1963
Mean	·19615

Temperature of jacket	21°·5 to 21°·6
Temperature of air near stem .	22·8 to 23·4
Temperature of 30,000-ohm coil.	21·5 to 22·3
Thermometer in calorimeter . .	Baudin 7320

Time.	Reading 7320.	Stem.	ΣΔ.	Time.	Reading 7320.	Stem.	ΣΔ.
m. s.	°			m. s.	°		
8 40	19·45	−·010	0	25 14	25·40	+·009	+·056
13 16	21·15	−·007	−·018	31 9	27·40	·021	·167
20 38	23·80	·000	+·005	35 58	28·98	·029	·299
25 14	25·40	+·009	·056	42 54	31·15	·039	·565

	2θ.	2θ'.	J.	
	51° 8'·4	7° 35'·6	41810000	
	50 57·5	7 28·5	41640000	
	50 48·5	7 24·4	41640000	
	50 40·4	7 21·4	41840000	

Time.	Galvanometer.	Time.	Galvanometer.
m. s.	° ′	m. s.	° ′
5 50	237 14	28 5	237 5
7 0	259 12	29 15	258 46
10 20	229 34	32 45	229 42
11 30	207 42	34 0	208 0
15 40	237 11	39 0	237 2
17 5	258 56	41 0	258 40
22 0	229 40	44 15	229 44
23 25	207 58	45 25	208 4

Following is the general Table of results:—

Date.........	Nov. 24.	Dec. 9.	Dec. 14.	Dec. 20.	Dec. 22.	Jan. 26.	Feb. 16.
Thermometer ...	7320	7320	6165	6165	6165	6165	6165
Temp. of water...	24°·3	25°·4	27°·0	26°·6	26°·3	27°·2	26°·2
Temp. of R′	23°·0	22°·1	23°·8	21°·7	23°·4	19° 1	20°·6
$\dfrac{J}{10000}$	4240 4248 4229 4274 4216 4217 4204 4225 4225 4224	4181 4164 4164 4184	4180 4222 4217	4207 4195 4206 4204 4182	4198 4216 4232 4218	4194 4192 4205 4193	4207 4219 4174
Means	4230	4173	4206	4199	4216	4196	4200

The greater number of results on Nov. 24 is due to the fact that single thermometer-readings were taken instead of groups.   The two experiments with 7320 show the greatest variation from the mean; but the mean of these two agrees closely with the general mean.   Experiments made on Nov. 29 and Dec. 6 were rejected on account of leakage of 3 and 6 grams respectively.   The results, however, are 4220 and 4227, falling within the limits of the series.   The duration of the experiment was less than one fifth of the interval between the two weighings of the calorimeter; and probably the loss during the experiment was the same fraction of the whole loss. Furthermore, the leakage during the radiation-experiment would affect the radiation-coefficient in such a manner as to approximately compensate for the effect of leakage during the main experiment.   For these reasons I have retained the experiments of Jan. 26 and Feb. 16, which showed a leakage of 1 gram and 1·5 gram respectively, but have given the results

half the weight of the other. The remaining experiments are satisfactory in this respect, the loss being a few tenths of a gram, due principally to the removal of the thermometer.

The result of the experiment is $J = 42,039,000$ O, where O is the value of one tenth of the 10-ohm coil in earth-quadrants per second. Reduced to the new value for the constant of the sine-galvanometer, it becomes $J = 42,055,000$ O.

I have also calculated the experiment from the formula $J = \dfrac{c^2 R t}{h}$, where R is the resistance of the calorimeter-coil as measured in the ordinary manner, corrected to the mean temperature of the water, and further corrected for superheating. I estimated the superheating from observations of the main and derived currents when the strength of the former was varied. The expression $\dfrac{c' R'}{c}$ should give the true resistance of the coil at any instant. When the currents are smaller, the superheating is less, and the comparison of the value of $\dfrac{c' R'}{c}$ for a zero-current, obtained by graphical extrapolation, with its value for the full current, should give the superheating. The method is not very accurate, as the observations with the smaller currents are uncertain. I find the increase of resistance due to superheating to be about 1 part in 700, corresponding to a difference of temperature of $2°$ C. When this correction is applied, the second method of calculation gives $J = 42,156,000$ O.

This result depends upon the square of the main current; and as the temperature of the coil changed $6°$ or $8°$ during the experiment, its mean resistance is somewhat uncertain. Hence this result has not the weight of the former.

The discovery of this discrepancy has greatly delayed the publication of this paper. It may be due to conduction to the water, which was guarded against by varnishing the wire and using distilled water, but was not proved to exist. For let E be the difference of potential of the ends of the coil, e the E.M.F. of polarization, R and r the resistances of coil and water respectively. Then the current in the coil is $C = \dfrac{E}{R}$, and the current in the water is $c = \dfrac{E - e}{r}$.

The energy converted into heat is

$$C^2 R + c^2 r = \frac{E^2}{R}\left[1 + \frac{R}{r}\left(1 - 2\,\frac{e}{E} + \frac{e^2}{E^2} \right) \right].$$

In the first method of calculation above the energy is com-

puted as

$$E(C+c)= \frac{E^2}{R}\left[1+ \frac{R}{r}\left(1- \frac{e}{E}\right)\right].$$

In the second method it is computed as

$$(C+c)^2R= \frac{E^2}{R}\left[1+ \frac{2R}{r}\left(1- \frac{e}{E}\right)\right] + \text{smaller terms.}$$

E was over 6 volts, e is about 1·5 volts. Hence the second result is larger than the first, which agrees with the facts, and the *error* of the first is less than one fourth of the difference between the two. The discussion shows that the first method of calculation is to be preferred; and I therefore take J = 42,055,000 O as the result.

Since the completion of my experiments, a 10-ohm Elliott standard in the possession of the University has been compared with the Cambridge standards and found correct at $20°·9$ C. My standard has been compared with this, with the following result:—

$$\frac{\text{W. M. \& C.'s coil}}{\text{Elliott's coil}} = 1·00168 \text{ in } 1878,$$

$$\qquad \text{''} \qquad \text{''} \quad = 1·00170 \text{ ,, } 1882,$$

$$\qquad \text{''} \qquad \text{''} \quad = 1·00173 \text{ ,, } 1883.$$

In these comparisons the Elliott coil was taken at $16°·3$ C., as marked. Also we have

$$\frac{\text{Elliott coil at } 20°·9}{\text{Elliott coil at } 16°·3} = 1·0014.$$

Hence $O= \frac{1·0017}{1·0014} = 1·0003$ B.A. units and J = 42,068,000 × value of B.A. unit in earth-quadrants per second.

Rowland[*] has discussed Joule's values, and reduced them to the air-thermometer and the latitude of Baltimore. The mean of the best results from the friction of water, in 1850 and 1878, thus becomes 426·55 kilogram-meters or 41,805,000 C.G.S. at $14°·1$ C. This, according to Rowland's results for the temperature-variation, corresponds to 41,608,000 at 26°, the mean temperature of my experiments. Rowland's value at 26° is 41,720,000. Combining the mean of these, 41,664,000, with my result, I find 1 B.A. unit $= \frac{41,664,000}{42,068,000} = ·9904$ earth-quadrant per second.

This research cannot compare in weight with the elaborate determinations of the ohm by direct methods which have been

* Proceedings of American Academy of Arts and Sciences, 1880.

made in England and this country since the conclusion of my experiments ; but as few results by this method are at hand, I publish it as a slight contribution to the history of this vexed subject.

Marlborough, N. Y., April 15, 1885.

II. *Summary of Lecture on Calculating Machines, delivered before the Physical Society of London, March 28, 1885, by* JOSEPH EDMONDSON, *of Halifax*[*].

CALCULATING machines are of two classes, the automatic and the semi-automatic. The former were invented by Mr. Charles Babbage between 1820 and 1834, and were designed mainly for the computation of tables. When the primary factors of a table are placed on such a machine, it will calculate the table and impress it line by line upon a stereo-mould with great celerity and absolute correctness. Mr. Babbage's machine, so far as it was completed, is in the South Kensington Museum ; and another machine by M. Scheutz (for the principles of which he confessed his indebtedness to Mr. Babbage) is in the office of the Registrar General at Somerset House. These machines proceed by the method of Differences, and are therefore termed " Difference-Engines." Their work is limited to addition, but they indirectly perform subtraction by adding the complement of the subtrahend.

If it be required to construct a table (of cubes for instance), the law of its growth must be found by reckoning mentally the first few terms of the table. Placing them in a line, the difference between each term and its successor is placed under the former. This process is repeated with the differences until at last a line is reached in which all the differences are cyphers. Thus :—

Table . . .	A	1	8	27	64	125	216
1st difference	B	7	19	37	61	91	
2nd „	C	12	18	24	30		
3rd „	D	6	6	6			
4th „	E	0	0				

The machine may now be set to work by placing the first column of figures in their respective places upon it. During the first half of the first revolution of the machine, the wheels containing the terms A and C have the terms B and D added on to them and become 8 and 18 respectively. During the second half-revolution, B and D have the terms C and E added on to them, becoming 19 and 6 respectively, and the second column is complete. Each succeeding revolution of the

[*] Communicated by the Physica Society.

machine similarly produces each succeeding column, the upper line being the term required for the table.

The apparatus consists of identical parts, equal in number to the digits required for the last column of the tables it is to compute. It is therefore very complex and very costly, and will not serve the purpose of computers in general, who must have recourse to the semi-automatic class of instruments. These are portable, of moderate cost, allow of very rapid working, and require no special mathematical skill.

In 1663 Sir Samuel Moreland produced an instrument by which additions and subtractions could be worked, digit by digit ; but it took more time than the ordinary mental operation. It was left to Viscount Mahon (afterwards Earl of Stanhope) to produce the first really practical instrument. Besides a machine dated 1780, which was a great advance on that of Sir Samuel Moreland, though on the same lines, he invented three machines. Those of 1775 and 1777 were on the table for inspection after the lecture, and abound in beautiful and effective contrivances. The third machine the lecturer had not seen, and it has never been described. In that of 1775 is found the " Stepped Reckoner," the basis of the only instruments that have come into extensive use.

The reckoner of the modern machines, patented in 1851 by M. Thomas de Colmar, consists of a cylinder divided into 10 sections, on which there are respectively 0, 1, 2, 3, 4, 5, 6, 7, 8, and 9 teeth. The teeth of one section being coincident with an equal number of those of the next section, the whole presents a stepped appearance. Each revolution of this reckoner moves a pinion of 10 teeth, in gear with one of its sections, as many teeth as there are upon that section. The motion of the pinion is communicated to a dial with the digits 0 to 9 in orderly succession upon it. Thus, if the figure seen through an aperture in the covering of the dial were 0, and the pinion were in gear with the section having 3 teeth, the first revolution of the reckoner would move the dial to 3 ; the second to 6 ; the third to 9 ; this result being the multiple of 3 (teeth on the reckoner) by 3 (revolutions). A series of, say, 8 reckoners, pinions and dials, each pinion being set to the section having 3 teeth, would give in 3 revolutions the product 99,999,999. The next revolution would bring in a new feature—the carrying of the tens. Here lies the great difficulty of Calculating Machines ; but the difficulty has been overcome, though not without leaving room for improvement. The 1 that will have to be carried from each dial to that immediately on its left cannot be added while the latter is being operated upon by its reckoner. The machine must therefore

make an independent note of it until it can be dealt with. Each dial has a tooth (the *primary* carrying-tooth) which makes this note at the moment that the dial passes from 9 to 0, by pushing along the axis of the reckoner belonging to the next higher digit a sliding-piece which revolves with the reckoner and carries a single tooth (the *secondary* carrying-tooth). Above this sliding-piece, and upon the same axis as the pinion in gear with the reckoner, is a second pinion of 10 teeth. Before the sliding-piece was moved by the primary carrying-tooth, the secondary carrying-tooth passed on the side of this second pinion without affecting it; but being now brought into line with it, the pinion will be moved 1 tooth, and will therefore add 1, as soon as the reckoner has added its own proper number; so that the fourth revolution, giving the product of 33,333,333 by 4, brings the dials to 133,333,332. When the secondary tooth has done its work, an incline on its side comes in contact with a projection on the frame of the machine, which restores it to its original inoperative position. Each reckoner is set to operate a little later than its neighbour to the right, so that the carrying on the latter may be completed before that on the former is commenced. The before-named blank space on the reckoner is to allow time for the carrying; and for a "dead-point" in the machine, at which the first-named pinions, which are movable longitudinally on their axes, may be set to their required sections of the reckoners, and other changes may be made in the setting of the machine. The position of the pinions is shown by indicators on the face of the machine, each of which can be set to any required figure.

Each pinion communicates its motion to its dial by bevel-gear in the well-known combination of three wheels, which permit the action to be reversed at will, so that the change from + to − or from × to ÷ is made instantaneously.

In multiplying by more than a single digit, the dials require to change their position in relation to the multiplicand, to imitate the "stepping" of the lines in long multiplication. They are therefore placed in a slide which can be moved, step by step, from right to left or *vice versâ*.

Up to a recent date the machine of M. Thomas de Colmar was the only one in use. A few years ago Mr. George B. Grant, of Boston, Mass., brought out an instrument somewhat on the lines of the Stanhope machine of 1777. It is very compact, is beautifully and substantially made; but as subtraction is performed by adding the complement of the subtrahend, reversing is so tedious as to be fatal to the general adoption of the machine. Its range is also very

limited, and there are other defects inherent in the method of its construction.

Still more recently Mr. Tate, of London, has introduced a machine on the lines of M. Thomas, in the internal mechanism of which there are several improvements. The workmanship, too, is very superior to that of the French instrument.

Mr. Edmondson (the lecturer) having, in practice, found certain inconvenient limits to the utility of these machines, conceived the idea of obviating them by throwing the instrument into the circular form, and thus obtaining an *endless* instead of a limited slide. This has produced a machine of greatly extended powers ; for it can deal with a multiplier or dividend of any number of figures, and can carry a quotient to any number of decimal places. But its chief utility does not consist in dealing with such large numbers. It frequently happens that quotients produced on a machine require to be further operated upon ; but as in the straight machines they are recorded on a special set of dials, which are not in the general working line, they must be transferred by hand before they can be dealt with in any other way than as multipliers. In the circular machine they come up in the working line ready for further operations. The circular form, in fact, gives a certain elasticity in the applications of the machine which could not be described within the limits of the lecture, and which can only be appreciated by actual use of the instrument. Although the special set of dials for recording multipliers and quotients are dispensed with as non-essential in the circular machine, they could be easily and conveniently added, and would still further extend the powers of the instrument.

The lecturer expressed his indebtedness to the following gentlemen for the loan of valuable instruments on the table, which, along with Mr. Tate's machine and several belonging to the lecturer himself, attracted much attention after the lecture :—

General Babbage, Bromley, Kent. A piece of the Difference-Engine of the late Charles Babbage, Esq. ; Stanhope Machines of 1775 and 1777 ; Sir Samuel Moreland's Machine of 1663.

The Rev. Professor Harley, F.R.S., Huddersfield. Stanhope Machine of 1780.

Theodore B. Jones, Esq., Harrogate. The American Machine of George B. Grant, Esq.

F. H. Bowman, Esq., D.Sc., Halifax. A Machine of Sir Samuel Moreland's, constructed on the principle of "Napier's Bones."

III. *On a New Law, analogous to those known under the names, Law of Avogadro and Law of Dulong and Petit.* By J. A. Groshans†.

WHEN the boiling-points and densities of substances are compared with their atomic composition, we find that there is a law regulating this relationship which is analogous to the laws mentioned in the title of this paper.

I have called this law, The Law of "Density Numbers." The density numbers (*Densitätzahlen*) form a new class of constants, which present themselves as attributes of the elements, and are of the following nature.

They are whole numbers. Each element possesses only one, which may be easily determined; but two or more elements may possess the same number.

Table I. contains a list of these new constants so far as they have yet been determined. An asterisk affixed to a number denotes that this is the number which appears to me probably the correct one, but that verification is necessary. I venture to hope that, when the scientific public realize the interesting nature of this new law, the constants given in the Table will be rigorously verified, and the gaps at present so numerous will then be filled up.

TABLE I.

Density-numbers of the Elements already determined.

C	1	Li	2	B*	3	F	4
H	1	Be	2	N	3	Na	4
O	1	S	2	P	3	Al	4
						Si	4
						Cl	4
Mg	5	Ca	7	V*	8	Cr	9
K	5			As	8	Mn	9
				Se	8	Fe	9
						Br	9
Ni	11			Sr	13	Zr*	14
Co	11			Nb*	13	Sn	14
Cu	11			Sb	13	Te	14
Zn	11					I	14
Rb*	11						
Pd*	16			Mo*	17	Ba	19
Ag	16			Cs*	17		
Cd	16						
Ta*	23			Hg	26	W*	29
Bi*	23			Tl*	26	Pt*	29
						Pb	29

† Communicated by the Author. Translated by W. W. J. Nicol, M.A., D.Sc., F.R.S.E.

The density-numbers of the elements increase with their atomic weights, but are *not* proportional to these.

The exact nature of these numbers is not yet distinctly made out; but the following provisional hypothesis, which, I believe, may ultimately prove to be correct, will help in forming a conception of their nature.

According to this hypothesis, carbon, hydrogen, and oxygen are simple bodies; but the other elements are compounds of other simple substances, the number of atoms of which is shown by the density-number of each element.

The law itself may be enunciated in the following simple form :—

" The densities of substances are proportional to the density-numbers."

For example, in the case of two compounds of carbon, hydrogen, and oxygen (comparable with one another), and with the formulæ $C_p H_q O_r$ and $C_{p'} H_{q'} O_{r'}$, if n and n' equal the sum of $p + q + r$ and $p' + q' + r'$ respectively, and the densities are δ and δ',

$$\frac{\delta}{\delta'} = \frac{n}{n'} \text{ or } \frac{n}{\delta} = \frac{n'}{\delta'} = \text{constant} = k.$$

The law of Avogadro leads in the same way to a constant; for if the vapour-density of a substance at $0°$ C. and 760 millim. equals D, and its molecular weight is a, then

$$\frac{D}{D'} = \frac{a}{a'}, \text{ whence } \frac{a}{D} = \text{constant}.$$

This constant is unique, and is true of all bodies which can be converted into vapour. Such is not the case, however, with the law of molecular specific heats ($a \times c$). This constant differs in the various groups of compounds; each group possesses a single constant which is peculiar to it. The law of density-numbers resembles in this respect that of Dulong and Petit.

This new law is applicable to substances in every state of aggregation; but it is necessary that the substances should be compared under similar conditions, such as :—

(1) as gases at the boiling-point;
(2) as liquids at the boiling-point;
(3) as solids (crystals hydrated or anhydrous);
(4) in very dilute solutions.

When dealing with substances which contain only carbon, hydrogen, and oxygen, I shall continue to use the letter n for the sum of the numbers of density; but when other elements enter into the composition of a body, I shall employ B to indicate the above sum.

In the following pages I shall endeavour to give a fairly complete account of the numerous applications of this law, the study of which has occupied my leisure hours for many years, ever since a happy chance disclosed to me a special case, an account of which was published in Poggendorff's *Annalen,* lxxviii. (1849) p. 112.

When the law is applied to hydrated crystalline salts containing the same number of molecules of water, a hitherto concealed relationship is discovered.

If B is the sum of the numbers of density of the salt, and δ its density, it is found that $\frac{B}{\delta} = k$ for all salts with similar formulæ and containing the same amount of water of crystallization, as will be seen from Table II., which contains the data relating to six salts of the general formula $MR_2 . 6H_2O$. B in this case is equal to the sum of the density-numbers for the anhydrous salt *plus* 18, which is the value of B or *n* for H_2O. Thus, a reference to Table I. shows that $CaCl_2\ 6H_2O$ has $B = 7 + 2(4) + 6(3) = 33$.

TABLE II.

Salt.	B.	δ.	k.
$SrCl_2$, 6 aq.........	$21 + 18 = 39$	1·964	19·86
$CaCl_2$　,,　.........	$15 + 18 = 33$	1·654	19·95
$CoCl_2$　,,　...	$19 + 18 = 37$	1·84	20·11
$MgCl_2$　,,　.........	$13 + 18 = 31$	1·562	19·85
$Ni(NO_3)_2$, 6 aq	$23 + 18 = 41$	2·05	20·00
$Zn(NO_3)_2$　,,　...	$23 + 18 = 41$	2·065	19·85

The data for this table and for others are taken from the collections made by Landolt and Börnstein, Clarke's 'Constants of Nature,' and the experiments of Bödeker, Playfair and Joule, Schröder, Topsoë, and others on the densities of compounds.

The table shows clearly enough that the volumes k are practically equal, and by means of such groups it is possible to determine the density-numbers for the various elements. All the density-numbers in Table I. have been determined by employing the data given by hydrated salts and (where possible) the boiling-points, and the densities of aqueous solutions as well as all other available analogous data.

At this point I shall return to Table I., in order to bring forward some views of a more general nature regarding the density-numbers.

Triads.

The name of Triads has been given to groups of elements such as chlorine, bromine, and iodine, or phosphorus, arsenic, and antimony ; and I shall retain the name, notwithstanding the fact that each group contains at least *four* elements. Of these four elements three are characteristic, while the fourth may be regarded as a *precursor*, which, although participating in the nature of the three principal elements, yet is distinct, and possesses properties more or less different.

The following table contains twenty elements arranged in five triads. I have chosen those which appear to be complete, and have added to the table the atomic weights and the density-numbers with their differences.

The density-numbers of the three principal elements in each triad have a constant difference, which is in two of the groups five units, in the other three six units.

TABLE III.—Triads.

No. 1.				No. 2.				No. 3.				No. 4.				No. 5.			
El.	AW.	B.	Δ.	El.	AW.	B.	Δ.	El.	AW.	B.	Δ.	El.	AW.	B.	Δ.	El.	AW.	B.	Δ.
N	14	3		O	16	1		F	19	4		Na	23	4		Mg	24	5	
			0				1				0				1				2
P	31	3		S	32	2		Cl	35·5	4		K	39	5		Ca	40	7	
			5				6				5				6				6
As	75	8		Se	79	8		Br	80	9		Rb	85	11		Sr	87·5	13	
			5				6				5				6				6
Sb	120	13		Te	125	14		I	127	14		Cs	133	17		Ba	137	19	

El = element.　AW = atomic weight.　B = density-number.
Δ = difference of density-numbers.

The differences in the atomic weights of the three principal elements all lie between 44 and 49·5. The equality of this difference in the same triad is only approximate; and the opinion, formerly held, of their exact equality has been rendered untenable by the experiments of Stas and Marignac, as shown in Table IV.

TABLE IV.

I.		II.		III.		IV.		V.	
P	31	S	32	Cl	35·5	K	39	Ca	40
	44		47		44·5		46·2		47·5
As	75	Se	79	Br	80	Rb	85·2	Sr	87·5
	45		46		47		47·5		49·5
Sb	120	Te	125	I	127	Cs	132·7	Ba	137

The differences in the atomic weights between the precursors and the first member of the triad proper varies from 16 to 17, and the difference in density-numbers from 0 to 2, as in Table V.

TABLE V.

Atomic Weights.				
I.	II.	III.	IV.	V.

N 14
    17
P 31
	O 16
	    16
	S 32
		F 19
		   16·5
		Cl 35·5
			Na 23
			    16
			K 39
				Mg 24
				    16
				Ca 40

Density-numbers.				

N=3
   0
P=3
	O=1
	   1
	S=2
		F =4
		   0
		Cl=4
			Na=4
			   1
			K =5
				Mg=5
				   2
				Ca =7

Among the elements in Table I., besides those included in the above triads, are to be found groups of two or more elements which present the same properties as the triads.

Thus there are three pairs with the difference 16.

TABLE VI.

Atomic weight.	Density-number.	Atomic weight.	Density-number.	Atomic weight.	Density-number.

Li 7
   16
Na 23
	2
	  2
	4
		B 11
		   16
		Al 27
			3
			  1
			4
				C 12
				   16
				Si 28
					1
					  3
					4

The difference of 16 in the atomic weights does not correspond to a constant difference in the density-numbers; but a difference of 45 to 48 corresponds to 5, as is seen in Table VII.

In the last pair (Ag, Tl) the differences are doubled.

TABLE VII.

Atomic weight.	Density-number.	Atomic weight.	Density-number.	Atomic weight.	Density-number.

Cu 63·5
   44·5
g 108
	11
	  5
	16
		Zn 65·5
		   46·5
		Cd 112
			11
			  5
			16
				Ag 108
				   96
				Tl 204
					16
					  10
					26

Again, comparing the pairs Hg and Zn, which are diad in compounds such as $Zn(C_2H_5)_2$, and Pb and Sn, which are

TABLE VIII.

Atomic weight.	Density-number.	Atomic weight.	Density-number.
Zn 65	11	Sn 118	14
135	15	89	15
Hg 200	26	Pb 207	29

tetrad in corresponding compounds, we find that in the first pair, where the difference in the atomic weights $135 = 3 \times 45$, that in the density-numbers $= 15 = 3 \times 5$; but that this is not the case with lead and tin; for while the difference in atomic weights $(= 89 = 2 \times 45)$ is double, the difference in density-numbers is treble. In time, I trust, as the gaps in Table I. are filled up, it will be possible to extend and generalize considerations of the above nature.

After this digression I shall return to the application of the law to hydrated crystals, and shall apply it to the results of the well-known experiments of Schiff on the density of alums and isomorphous sulphates.

TABLE IX.

Experiments of Schiff.

Salts.	B.	δ.	k.
(a) Alums:—			
AlK (SO$_4$)$_2$ 12H$_2$O	57	1·722	33·1
AlNa(SO$_4$)$_2$ „	56	1·641	34·1
CrK (SO$_4$)$_2$ „	62	1·845	33·6
(b) Sulphates:—			
MgSO$_4$ 7H$_2$O	32	1·685	19·0
Zn SO$_4$ „	38	1·953	19·5
Ni SO$_4$ „	38	1·931	19·7
Co SO$_4$ „	38	1·924	19·8
Fe SO$_4$ „	36	1·884	19·1
(c) Double Sulphates:—			
MgK$_2$(SO$_4$)$_2$ 6H$_2$O	45	1·995	22·4
ZnK$_2$ (SO$_4$)$_2$ „	51	2·153	23·7
NiK$_2$ (SO$_4$)$_2$ „	51	2·123	24·0
CoK$_2$ (SO$_4$)$_2$ „	51	2·154	23·7
FeK$_2$ (SO$_4$)$_2$ „	49	2·189	22·4
CdK$_2$ (SO$_4$)$_2$ „	56	2·438	23·0
CuK$_2$ (SO$_4$)$_2$ „	51	2·137	23·9

I have omitted from the table the data for the compounds in which potassium is replaced by ammonium. The value of k is here also constant, but slightly greater than that for the potassium compounds. The salts here considered have approximately equal molecular volumes*. Thus the alums are thus related :—

	Atomic weight.	δ.	Molecular volume.
AlK $(SO_4)_2$ $12H_2O$	474	1·722	275·3
AlNa$(SO_4)_2$ $12H_2O$	458	1·641	279·1
CrK $(SO_4)_2$ $12H_2O$	499	1·845	270·5

Application of the Law to Bodies in Vapour at the Boiling-point.

If the boiling-point be $s°$ Centigrade, and Ds be the density of the vapour at that temperature, the pressure being 760 millim., then $T = 273 + s°$; and the laws of Avogadro and Gay-Lussac may be expressed thus :—

$$\frac{Ds}{D's'} = \frac{a}{a'} \times \frac{T'}{T}.$$

On the other hand, the law of density-numbers gives

$$\frac{Ds}{D's'} = \frac{B}{B'}.$$

Hence it follows that

$$\frac{TB}{a} = \text{constant} ;$$

or, for bodies containing only carbon, hydrogen, and oxygen,

$$\frac{T \times n}{a} = \text{constant (see above).}$$

---

* The equality (approximate) of the molecular volumes of isomorphous bodies, which was long ago recognized, may be regarded as to some extent an anticipation of the law of density-numbers, and may be explained as follows:—

The constants $k = \dfrac{B}{\delta}$ are equal according to the law. In certain cases (such as the salts in the table) the relation $\left(\dfrac{a}{B}\right)$ between the atomic weight and the density-numbers is nearly the same for different members of the same group; hence it follows that the values of $\dfrac{a}{\delta}$ (that is, the molecular volumes) are approximately equal.

The value of this constant for water (density-number $=3$) is

$$\frac{273 + 100 \times 3}{18} = 62 \cdot 2.$$

In Table X. are given the data relating to 13 substances which contain $C_p H_q O_r$, the value of q being in the first group 10, in the second 8.

<center>TABLE X.</center>

<center>Constant $Tn/a = 62 \cdot 2$.</center>

Name.	Formula.	a.	n.	S°.	T.	Tn/a.
Ethylic ether...............	$C_4H_{10}O$	74	15	34	308	62·4
Ethyl allyl ether	$C_5H_{10}O$	86	16	64	337	62·7
Ethyl propionate	$C_5H_{10}O_2$	102	17	100	373	62·2
Ethyl carbonate	$C_5H_{10}O_3$	118	18	126	399	60·9
Allylic ether	$C_6H_{10}O$	98	17	86	359	62·3
Allylic propionate	$C_6H_{10}O_2$	114	18	123	396	62·5
Ethylic oxalate	$C_6H_{10}O_4$	146	20	186	459	62·9
Allyl oxalate...............	$C_8H_{10}O_4$	170	22	206	479	62·0
Toluene	C_7H_8	92	15	108	381	62·1
Anisol	C_7H_8O	103	16	150	423	62·6
Ethyl pyromuconate ...	$C_7H_8O_3$	140	18	209	452	62·0
Methyl benzoate	$C_8H_8O_2$	136	18	198	471	62·3
Methyl salicylate	$C_8H_8O_3$	152	19	223	496	62·0

Table XI. comprises substances with fourteen atoms of hydrogen. The constant $\dfrac{Tn}{a}$ is different from that in Table X., but is here the same for all the bodies.

<center>TABLE XI.</center>

Names.	C.	H.	O.	a.	n.	S°.	Authorities.	Tn/a.
Hexane	6	14	...	86	20	45	Go.*	73·9
Ethyl propylate	6	14	1	102	21	85	Ch.	73·7
Diethyl glycol	6	14	2	118	22	123	Wö.	73·9
Ethyl valerate	7	14	2	130	23	143	Li.	73·6
Allyl valerate	8	14	2	142	24	165	Wü.	74·0
Ethyl ethylacetocarbonate	8	14	3	158	25	195	Wö.	74·0
Ethyl succinate..................	8	14	4	174	26	217	Kp.	73·2
Diethylene diacetate	8	14	5	190	27	248	Wö.	74·0
Allyl acetoacetate.................	9	14	3	170	26	206	Wö.	73·3
Ethyl itaconate..................	9	14	4	186	27	227	Ke.	72·6

<center>Mean value of $\dfrac{Tn}{a} = 73 \cdot 6$.</center>

* Go. means Goriainow; Ch. = Chancel; Wö. = Dictionary Fehling; Li. = Linnemann; Wü. = Dictionary Würtz; Kp. = Kopp; Ke. = Kékulé, Lehrbuch.

Connection between the different Values of the Constant $\dfrac{Tn}{a}$.

In an homologous series one observes generally certain properties common to all the members ; *e. g.* :—

(1) A regular increase in the boiling-points of the successive members of the same series.

(2) The amount of this increase varies slightly, but is from 16° to 20° for every addition of the group CH_2. It was formerly supposed that the differences were equal ; but, so far as experiment has gone, we are able to point to only approximate equality.

In order to apply the law of density-numbers to homologous series, it will be convenient to number the members of a series 1, 2, 3, &c., according to the place in the series occupied by each. I shall call these numbers m : thus benzol has $m=4$; it is therefore the fourth member of its series according to the new Law, though at present the first one known*.

Table XI. contains the substances each containing fourteen atoms of hydrogen ; each is the seventh member of its respective series, for m here equals 7. Such substances I shall call " corresponding " compounds. They have, as a rule, similar properties, and have frequently the same constants Tn/a.

I may now sum up the results of observations on the constants $\dfrac{Tn}{a}$ as follows :—

(1) These constants, of which we have already met two (62·2 and 73·6), form an algebraic series of numbers which are the same for all bodies, whether metals or non-metals, and their compounds.

(2) In an homologous series the constants increase with the successive additions of CH_2, *i. e.* with the value of m.

(3) There are numerous homologous series the corresponding members of which possess the same constant, *e. g.* :—

a. Ethers	.	.	$C_n H_{2n} O_2$,
β. ,,	.	.	$C_n H_{2n-2} O_4$.
γ. ,,	.	.	$C_n H_{2n+2} O$.
δ. Benzol &c.			$C_n H_{2n-6}$.

---

* M. Groshans has not made it quite clear how he obtains the numbers m otherwise than by experiment. They are found in compounds of carbon, hydrogen, and oxygen by dividing the carbon and hydrogen by the group CH_2 and adding one to the number thus obtained ; the residue left, after deducting all the CH_2 groups, being the *first* body : thus ether, $C_4 H_{10} O$, is the fifth, for it $= 4(CH_2) + H_2O$, and H_2O is the first of the series $C_n H_{2n+2} O$.— *Translator.*

(4) A comparison of the constants of these four series and of many others has shown that it is possible to express the series of constants $\dfrac{Tn}{a}$ by the formula

$$\frac{Tn}{a} = 27\cdot8 . \sqrt{x},$$

where $x = 1, 2, 3, 4,$ &c.

(5) In the four series above,

$$x = m ;$$

but in other series,

$$x = m + y,$$

y being a small number; thus, in the ethylic alcohol series,

$$x = m + 3.$$

The constant $\dfrac{Tn}{a}$ in Table X. corresponds to $x = 5$. It is also the constant for water, and it is for this reason that I have adopted the value $27\cdot8$. For with water we have

$$(273 + 100) \frac{3}{18} \times \frac{1}{\sqrt{5}} = 27\cdot801.$$

On this basis are calculated the constants for various values of x given in Table XII.

TABLE XII.

x.	Tn/a.	x.	Tn/a.	x.	Tn/a.
1.	27·80	4.	55·60	7.	73·56
2.	39·32	5.	62·17	8.	78·63
3.	48·15	6.	68·10	9.	83·41

In the following table are given the boiling-points, observed and calculated, for the first sixteen ethers of the series $C_n H_{2n} O_2$. The formula used in the calculation is

$$T = (273 + s) = \frac{a}{n} 27\cdot8 \sqrt{m}.$$

TABLE XIII.

Boiling-points (*s*), observed and calculated, for the Ethers $C_n H_{2n} O_2$.

m.	Formulæ.	a.	n.	S°, observed.	S°, calculated.	Differences.	Authorities.
1.	(C H$_2$ O$_2$)	46	5	......	−17·2		
2.	C$_2$ H$_4$ O$_2$	60	8	33	+21·8	39	Kp.*
3.	C$_3$ H$_6$ O$_2$	74	11	53	51·0	29·2	Pi.
4.	C$_4$ H$_8$ O$_2$	88	14	77	76·6	25·6	Li.
5.	C$_5$ H$_{10}$O$_2$	102	17	100	100	23·4	Pu.
6.	C$_6$ H$_{12}$O$_2$	116	20	122	122·0	22·0	Li.
7.	C$_7$ H$_{14}$O$_2$	130	23	143	142·7	20·7	Li.
8.	C$_8$ H$_{16}$O$_2$	144	26	162	162·5	19·8	Fe.
9.	C$_9$ H$_{18}$O$_2$	158	29	176	181·5	19·0	Wö.
10.	C$_{10}$H$_{20}$O$_2$	172	32	200	199·6	18·1	Sch.
11.	C$_{11}$H$_{22}$O$_2$	186	35	217	217·0	17·4	Ca.
12.	(C$_{12}$H$_{24}$O$_2$)	200	38	......	233·9	16·9	
13.	C$_{13}$H$_{26}$O$_2$	214	41	250	250·3	16·4	Zi.
14.	C$_{14}$H$_{28}$O$_2$	228	44	269	266·1	15·8	Zi.
15.	(C$_{15}$H$_{30}$O$_2$)	242	47	......	281·5	15·4	
16.	C$_{16}$H$_{32}$O$_2$	256	50	298	296·7	15·2	Zi.

TABLE XIV.

Boiling-points, calculated and observed, of Benzol and its Homologues.

m.	Name.	Formula.	a.	n.	S°, observed.	S°, calculated.	Differences of s°.	Authorities.
1.	....	C$_3$	36	3	......	60·7		
2.	....	C$_4$ H$_2$	50	6	... ...	54·7	15·1	
3.	....	C$_5$ H$_4$	64	9	......	69·8	18·7	
4.	Benzol ...	C$_6$ H$_6$	78	12	85	88·5	19·0	Henry.
5.	Toluol ...	C$_7$ H$_8$	92	15	108	108·4	19·7	Noad.
6.	Xylol	C$_8$ H$_{10}$	106	18	129	128·1	19·4	Cahours.
7.	Cumol	C$_9$ H$_{12}$	120	21	152	147·5	18·7	Gerhardt.
8.	Cymol ...	C$_{10}$H$_{14}$	134	24	171	166·2	18·0	Noad.
9.	Laurol ...	C$_{11}$H$_{16}$	148	27	188	184·2		Fittig.

In the columns headed " differences " in the last two tables I have given the increase of calculated boiling-point for each successive member of the series, and a similar relationship is to be found in the case of other series.   Thus, in :—

* Kp. stands for Kopp; Pi. = Pierre; Li. = Linnemann; Pu. = Puchot; Fe. = Fehling; Wö. = Wörterbuch (dictionary) Fehling Sch. = Schorlemmer; Ca. = Cahours; Zi. = Zincke.

(1) The Ethers $C_n H_{2n+2} O$, beginning with $C_3 H_8 O$, where x is equal to $m=4$, the differences are:—

$$27\cdot6, \quad 26\cdot3, \quad 24\cdot5, \quad 22\cdot8, \quad 21\cdot3, \quad 20\cdot5, \quad 19\cdot5.$$

(2) The series beginning with Methyl Benzoate, $C_8 H_8 O_2$, where $x=m=5$,

$$16\cdot7, \quad 16\cdot2, \quad 15\cdot8, \quad 15\cdot4, \quad 15\cdot0.$$

(3) The Alcohol series $C_n H_{2n+2} O$, beginning with $CH_4 O$, where $x=m+3=5$,

$$16\cdot6, \quad 19\cdot6, \quad 20\cdot2, \quad 19\cdot8, \quad 19\cdot4, \quad 18\cdot6, \quad 17\cdot9.$$

The first three substances in Table XIV. do not exist, and it is very commonly found that the first members of homologous series, those corresponding to $m=(1)$, (2), (3), are wanting. There are, however, cases where similar bodies are to be met with : thus the series $C_n H_{2n+2}$ gives rise by substitution to $C_n H_{2n+1}Cl$ and $C_n H_{2n}Cl_2$. And all the corresponding members of the three series possess the same constants : $T n/a$ (or $T B/a$) and $V s n/a$ (or $V s B/a$).

The first members of the substituted series are chlorine and hydrochloric acid, which both have $x=1$[*].

As a general rule, the value of x is a whole number, but it sometimes happens that this is not the case. Thus, $x=3\frac{1}{2}$ for acetic acid, $C_2 H_4 O_2$; acetic anhydride, $C_4 H_6 O_3$; and a similar substance differing from the anhydride in possessing one atom of oxygen more, $C_4 H_6 O_4$, methyl oxalate. All the three are well known to behave anomalously. Thus the vapour-density of acetic acid is abnormal. All three are solid at temperatures below which their higher homologues are still liquid ; and, finally, the aqueous solution of acetic acid is remarkable for possessing a maximum of density at 80 per cent.

<div align="center">[To be continued.]</div>

---

[*] With regard to gases such as oxygen, and some others such as CO, CO_2, SO_2, CS_2, &c., we find that the value of x is a fraction much less than unity.

Just as experiment has shown that there are cases to which the laws of Avogadro and those analogous to it are not applicable, so we find similar cases in which the law of density-numbers no longer holds good.

IV. *On Colliding Water-jets.*
By H. Frank. Newall, *M.A.**

LORD RAYLEIGH has recently (Proc. R. S. vols. xxviii., xxix. 1879, and vol. xxxiv. 1882) investigated many of the phenomena of liquid jets. I will recall one form of experiment, and record an observation and a few experiments bearing on it.

Two horizontal jets of water, issuing from similar glass nozzles and fed from two glass bottles, are made to collide at a small angle. When certain precautions are taken, such as using clean and tolerably dust-free water, the jets rebound from one another ; but they are made to unite if each bottle is connected with the pole of a cell (such as Grove's or Leclanché's). It is convenient to introduce a key.

I have lately, in repeating this experiment, observed that the colours of thin plates (Newton's Rings) are formed with remarkable brilliancy between the colliding jets. The jets are of circular section, but on impact they become flattened against one another, so that the surfaces of separation are more or less plane, and vertical. Between these surfaces, which Lord Rayleigh has shown to be electrically insulated from one another, there is a very thin film (of air, I presume) in which the colours are visible. These afford a mode of observation by which one may possibly gain information as to the nature of the action of electricity in determining the coalescence of the jets.

I will first describe the appearance of the colours. The case I have examined most carefully is that when the jets start in the same horizontal plane and the surfaces of separation of the colliding jets are vertical. There is some difficulty in getting a good view of the colours, on account of the corrugations produced in the jets at collision. I have found it best to take the plane of incidence of the light horizontal, and to let the light fall *against* the direction of the water in the jets, and very nearly at normal incidence ; and I use a magnifying-glass to observe with.

The figure shows the appearance of the jets about the place of collision, the bold lines denoting outline and marks on the near surface ; the dotted lines show the isochromatic curves : those to the right are those which seem to be least distorted by refraction. The bold lines at R show the small stationary ripples on the cylindrical surface of the jet just before the

point of collision. The jets come from the right, as shown by the arrow.

The form of the isochromatic curves is more or less constant in character, though the colouring of the figures varies with the velocity of the jets and the angle at which they collide; increase in either of these conditions lowers the order of the colours produced, as is to be expected. There is a certain symmetry in the figure, more marked on the right than elsewhere. I describe a particular case, which may be taken as a sample of the general appearances.

Starting, then, from the right, close up to the ripples R, there appears green of the fifth order in a straight line perpendicular to the axis of the jet, as shown at 1. The colours of higher order I have not made out, on account of the ripples. The line 2 is red of fourth order; line 3 green of fourth
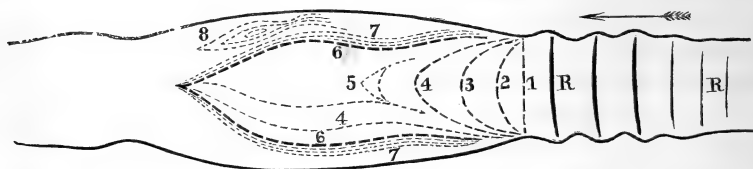
order; lines 4 are red of the third order. Here the symmetry in colour ceases. Lines 5 show yellow of the third order; and line 6 blue of the third order. The curves appear to be drawn in to a point on the left; but this I take to be an effect due to refraction through the uneven thickness of the flattened jet. These broader bands of colour are bordered at top and bottom by the colours of higher order succeeding very closely on one another, as suggested in the figure by the lines 7; and towards the left at the top, 8, there appear rings, which I imagine are probably seen reflected from within the nearer jet.

It is necessary to see that the tubes leading the water from the bottles to the nozzles are kept quite still; otherwise there are irregularities in the velocity of the jets which give rise to flickering in the colours. And in order to keep the conditions of collision as nearly the same as possible throughout one set of observations, it will also be found convenient to separate the jets, if they coalesce, by holding an electrified stick of sealing-wax close to either of the jets for a moment.

Having thus found means of avoiding changes in the colours, I proceeded to test the effect of gradually increasing from zero an electromotive force across the film of air between the rebounding jets, by connecting the water in the bottles elec-

trically with different points on a fine wire, which carries the current between the poles of a bichromate cell. I have examined the cases when the colours are of tolerably low order, that is when the separating film is thin ; and I have not been able to detect any change of colours, pointing to the gradual approach of the jets. The colours remain constant, until the electromotive force is raised to such a point that coalescence takes place ; and then they disappear quite suddenly. I had determined to give the matter one more trial, wishing to observe the effects when the jets collide at an extremely small angle. In this case it may be arranged that the colours produced are not of lower order than the fourth in the thinnest part of the film. This would be the most delicate means of testing. But I have been completely foiled in my attempts ; for the jets persistently refuse to rebound from one another for longer periods than a small fraction of a second. I attribute this to the large amount of pollen in the air, blown from fir-trees near the house ; for I find quantities of golden powder collected on my table and elsewhere in the house.

My observations then, so far as they have gone, eliminate conclusively the explanation, which Lord Rayleigh has referred to as *possible* though not probable, namely that the action of electricity in promoting union may be ascribed to the "additional pressure called into play by electrical attraction of the opposed water-surfaces, acting as plates of a condenser" (Proc. Roy. Soc. vol. xxxiv. p. 145).

The extraordinary capriciousness of union—the jets sometimes coalescing with very much smaller electromotive forces than at other times—made me for a time think that dust might still be at work ; that the dust, which in the ordinary state of the jets is not able to cause coalescence, might, under the possibly directive influence of the electromotive force (much as in an experiment described by Faraday), be turned across the separating surfaces of the jets, and so rupture them. If this were the case, one would expect that a larger electromotive force would be required to bring about coalescence, when the water supplying the jets had been allowed to settle. I left the water for five days to settle and found no appreciable difference between the electromotive forces required to produce union, when this "settled" water was used, and when dusty water was used immediately afterwards. Nor did diminution in the velocity of the jets affect the magnitude of the requisite electromotive force.

Lord Rayleigh regards the union as most probably due to perforation of the separating skin, brought about by disruptive discharge. Let us consider the case when the colour of

lowest order produced in the film between the jets is green of the third order at normal incidence : the thickness of the film is, roughly speaking, $2\frac{1}{2}/2 \times 6000 \times 10^{-8}$ centims., that is 0·000075 centims.   It appears that the highest minimum electromotive force to produce union is about 0·75 volt.   This gives a difference of potential in volts per centimetre of 10,000. Now Sir W. Thomson's experiments show that, to produce a spark between brass plates nearly 100 times further apart than the jets in the case we are considering, an electromotive force at the rate of about 80,000 volts per centimetre is required.   De La Rue and Müller have lately shown that the substitution of saturated aqueous vapour for dry air between the plates does not make any great difference.   It is, however, conceivable that there is diminished pressure between the jets.

Crowthorne, Wokingham, June 1885.

V. *Observations on the Electrical Processes in Thunder-clouds.* By Julius Elster *and* Hans Geitel[*].

IN an investigation, with which we have been some time engaged, on the production of electricity by the friction of finely divided liquids against solids of various temperatures, we had occasion to observe the exceeding sensitiveness to electrical induction of disintegrating jets of liquid as well as of all solid and liquid particles suspended in a current of air. This action is the chief source of error to be contended against in such experiments ; and, as we shall have occasion to show in a subsequent paper, it makes it very difficult to settle the question whether electricity is produced when water-spray rubs against *cold* bodies.   The phenomenon has long been known for jets of liquid, and has already had a practical application in Thomson's drop-collector and the water-induction machine.   It was an obvious idea to consider that inductive actions of a similar kind are also at work in the processes which take place in a thunder-cloud—that is, just to regard the latter as a self-acting duplicator.

The principle of this idea will be best seen from an experiment which can be made by the simplest means.

A cylindrical metal tube, A, open at both ends (about 50 centim. long and 8 centim. in diameter), is fixed vertically to a lateral insulated holder.   A small vessel, B, which is also cylindrical, can be inserted from the top, being held by an insulated handle.   This latter vessel is closed below, and is

provided with an efflux-tube directed downwards and ending in a narrow aperture. If now a small charge of + electricity is imparted to the tube A, while at the same time the insulated vessel B filled with water is held over it, the drops from B become negatively electrified, but fall through the tube A without coming in contact with the sides. By this means B itself is positively charged, and in an extremely short time acquires a potential which is not much lower than that of A, when the difference between B and A is not too great. If now B, while still held by the insulating handle, is rapidly inserted in A, and touches it momentarily, the electricity of B passes almost completely over to A, according to known electrostatic laws. If B be withdrawn to its original position, the same operation may be repeated. It must be remembered that A has now a greater charge than before, and that accordingly B is also more strongly influenced. It follows accordingly that, by repeating the operation, the charge of A increases in geometrical progression. In practice the limit is soon reached. With such a duplicator it is easy to show a considerable increase in the strength of the charge; it is only necessary to connect A during the experiment with a gold-leaf electroscope and to be somewhat quick in moving B. We observed almost always a self-excitation of the apparatus, so that after fortyfold oscillation of the vessel B a spark could be taken from the tube A.

The process in a thunder-cloud may be considered to be analogous. Suppose that a given charge of + electricity is imparted to one place in the lower layer. As long as the cloud is not dissolved in rain this electricity remains in nearly the same place, or only slowly spreads with decreasing potential over the entire cloud according to the conductivity of the mass of vapour. The case is different when the cloud dissolves in rain, where it may be assumed that the formation of drops must take place in the upper, that is the colder, layers of air. As far as the cloud rains it will acquire positive electricity ; and if the formation of rain does not begin at too great a height above the electrical layer, it is of not much lower potential than the latter. The negatively electrified drops fall to the earth through the lower inducing layer.

But now, as has often been pointed out (so far as we know, first by Hermann J. Klein), the contraction of surface, which accompanies the formation of rain, must produce an increase of potential. As the entire mass of cloud which was previously charged with positive electricity by induction aggregates together, and the individual particles of vapour coalesce to form larger drops, the electricity is confined with increasing

potential to a smaller space, and must again act by induction and with increasing power on the newly formed masses of clouds. As soon as the formation of rain begins in these the same process is repeated ; by a further aggregation of the clouds a fresh increase of potential is produced, and so forth. It can easily be conceived that in this way the electrical potential of a rain-cloud may go on increasing until discharge takes place.

In the experiment just described the vessel A represents the lower inducing layer of cloud ; B the upper rainy part of the same. The contraction of surface, although corresponding but little to the actual process in the thunder-cloud, is reproduced by the introduction of the vessel B into A.

The question of the origin of the initial charge of the lower layer of cloud will not be so easy to answer. In any case a *very small* potential will be sufficient, with a heavy rainfall, to be increased to the greatest amount. It is perhaps the ordinary atmospheric electricity which, passing to the clouds, produces a greater local charge. Without being kept up by the fall of rain, the strongest charge would not last. To look upon the condensation of aqueous vapour in itself as a source of electricity appears to us inadmissible, as it is not clear in what way the separation of the electricities can take place in this process. Friction can only explain the *initial charge*, and is quite inadequate to account for the enormous disengagement of electricity which takes place in nature. We might, moreover, think of a friction of fine aqueous vapour against large drops or against hailstones. It is not improbable that the difference between the capillary superficial tension of the smallest and largest drops of water may in friction produce a separation of the electricities ; but in any case such an excitation has not been ascertained with certainty. Supposing it, however, to be so, is the *vis viva* lost in this friction sufficient to produce the mechanical equivalent of even one flash ?

It might be urged against the above view, that the diminution in volume of a cloud consists essentially in the coalescence of particles of vapour to form larger drops ; that therefore the electricity must accumulate on the latter, and ultimately be carried away with it as it falls. This is undoubtedly partially the case. We must, however, remember that for a certain time the drops which form in the lower layer of cloud must be supported by the ascending current of air, the force of which must decrease with the height ; while the drops which come from the *upper* layers must reach the lower layers with greater velocity, and consequently must more easily

overcome the resistance of the ascending air. Part of the charge is thus lost, but the part is smaller the more powerful is the ascending current. There is, moreover, a continual replacement, owing to uninterrupted condensation.

With very fine rain, which at once falls to the earth, powerful charges will scarcely be expected. Much depends, in any case, on the rapidity of the formation of clouds and rain. The rain which falls from a cloud must have the opposite electricity to the cloud, and can of course act by induction on a second cloud which it traverses, and which also rains.

Moreover, after each flash of lightning the remainder of the electricity will soon attain a maximum if the rainfall is sufficient, and the contraction in volume which is inseparable from it.

The essence of this theory is that the electricity of thunder-clouds acts by induction, and that the thunder-cloud is a self-acting duplicator. The rain which falls from it plays the part of the jet of water in Thomson's drop-accumulator, while the increase of potential is occasioned by the enormous contraction of volume and surface.

This theory may claim over preceding ones the following advantages :—

(1) It enables us to regard the cloud as an aggregate of discrete drops of water. Hence a charge imparted to a cloud does not spread by conduction, but as soon as the cloud begins to rain spreads from point to point by induction.

(2) It does not require electrification by friction. It is not impossible that friction may give the start ; but this becomes unimportant in the further progress of the phenomenon. If it should come out, and a number of experiments we have tried do not allow us to settle the point, that a production of electricity by the friction of water-spray or rain against water or ice cannot be experimentally proved, the presence of atmospheric electricity is sufficient to start the phenomenon.

(3) The theory finds the equivalent of the work expended, in the establishment of a difference of potential, in the *vis viva* of the falling drops of water.

VI. *On certain Cases of Electrolytic Decomposition.*   *By* J. W. CLARK, *Assistant Professor of Physics in University College, Liverpool*[*].

THE atomic or molecular conditions which determine metallic or electrolytic conduction are of great interest, but seem as yet too obscure to allow of any definite general conclu-

[*] Communicated by the Physical Society : read May 23, 1885.

sions respecting their nature, beyond regarding a free motion of the particles resulting either from fusion or from solution as necessary for electrolytic conduction. Even this is not without noteworthy exceptions; for Faraday has described some binary compound liquids ($SnCl_4$, $AsCl_3$, &c.[*]) which neither conduct nor decompose; whilst, on the other hand, some compound solids are known which conduct metallically (Cu_2Se[†], Ag_2Se[†], SnS_2, CuS[†], to which perhaps must be added PbO_2, MnO_2, and Ag_2O), and some bodies which are solid and yet conduct electrolytically (Cu_2S[‡], Ag_2S[§]). Further, zincic iodide[§] neither conducts nor is decomposed when rendered fluid by heat; whilst others (HgI_2[§], $HgCl_2$[§], $PbFl_2$[‖]) have been considered as conducting without decomposition under the same circumstances. The nature of the conduction of the metallic sulphides is very imperfectly known[¶].

Whilst thinking over these facts about a year and a half ago, it seemed to me very probable that a careful study of these exceptions to the general laws of electrolytic decomposition might result in more definite conjectures respecting the condition of internal or molecular structure required for conduction and decomposition. To make such a study complete requires the determination and comparison of a number of physical constants (*e. g.* colour, conductivity, expansion, specific and latent heat, refractive index, specific inductive capacity, &c.) for substances which are normal and abnormal in their electrolytic behaviour. This cannot be completely done at present for want of data; but before passing to the consideration of those bodies to which my own investigation refers, I wish to briefly refer to a few previous papers relating to substances of remarkable electrolytic behaviour from this point of view.

Hittorf states that sulphide of silver fuses at a clear red heat, but at a temperature of 180° C. it is sufficiently soft to adapt its shape slowly to that of the surface upon which it rests, and at the ordinary temperature it is malleable: a cast stick of it can be slightly bent without fracture, and it can be cut with a knife or turned in a lathe. This substance has a very low resistance, and even at the ordinary temperatures is electrolytically decomposable by a feeble current. Hittorf (*l. c.*) has concluded, from a long and careful series of experiments upon it, that it conducts electrolytically only, and that

---

* Faraday, 'Experimental Researches,' vol. i.
† Hittorf, Pogg. *Ann.* Bd. lxxxiv. 1851.   ‡ Hittorf (*l. c.*).   § Faraday.
‖ Faraday.   Beetz (Pogg. *Ann.* Bd. xcii. 1854) has since shown that conduction takes place in a normal electrolytic way. Faraday discovered that the solid Plumbic Fluoride began to conduct below a red heat.
¶ See Faraday, 'Experimental Researches'; and Hittorf (*l. c.*).

its apparent metallic conduction results when a fine thread of metallic silver has formed between the terminals of the sulphide of silver bar.

Hittorf (*l. c.*) has discovered that cuprous sulphide also conducts electrolytically " und besitzt entweder gar keine oder ganz geringe metallische Leitung." Unlike sulphide of silver this body has a high resistance, but, like it, the conductivity increases with increased temperature. Cuprous sulphide melts at a white heat, and may be cast in the form of a rod which at the ordinary temperature is very brittle, although at a " higher" temperature it may be bent.

Hittorf (*l. c.*) points out the difficulty of proving *experimentally* that the conduction of Cu_2S and Ag_2S is *entirely* electrolytic, because the formation of copper or silver by the action of the current in the substance of the bars places their ends in true metallic communication with the battery-terminals.

Cuprous selenide and argentic selenide closely resemble their corresponding sulphur compounds to which reference has just been made, and are described as being " soft" and " slightly malleable" respectively (Watts's ' Dictionary of Chemistry '). Selenides ordinarily closely resemble sulphides in their physical and chemical relations, and are consequently regarded as being possessed of similar molecular constitutions. Hittorf, however, says of cuprous and of argentic selenide, that " beide sind gute metallische Leiter." Their electrical behaviour is therefore of an exactly opposite nature to that of their corresponding sulphur compounds.

Faraday has noticed that conduction commences in heated electrolytes at very different degrees of liquefaction and softening.

Plumbic chloride * conducts very appreciably at a temperature far below that at which it fuses, and at which it is not noticeably soft. Beetz (*l. c.*) has shown that glass begins to conduct between 200° C. and 220° C., and Dr. Lodge reminds me that this has recently been shown to take place at 100° C.

It appears from the behaviour of these bodies that—

(i.) *In some solid electrolytes there is a sufficient mobility of the molecules at the ordinary temperature to enable electrolytic conduction to take place; in others it is conferred by a rise of temperature which is insufficient to render the solid liquid or even*

---

* E. Wiedemann, *Ber. d. Kgl. Sachs. Gesellschaft der Wissenschaften,* 1874. I have unfortunately been unable to refer to this paper; but since the above was written the author has kindly referred me to ' Die Elektricitätslehrer ' (G. Wiedemann), Bd. i. S. 558, wherein it is stated that the iodide and bromide of lead behave similarly.

soft. *A rise of temperature which is insufficient to render a solid liquid, or so soft as to change its shape, is also sufficient for the equalization of strain as is shown in the annealing of glass. Both electrolytic conduction and the annealing of glass take place more readily at a high than at a low temperature.*

(ii.) *Substances of apparently similar constitution may exhibit opposite forms of electrical conduction* (Cu_2Se, Ag_2Se, and Ag_2S, Cu_2S).

The bodies to which my investigation refers are mercuric chloride and mercuric iodide, which Faraday believed to conduct metallically in the fused condition.

Beetz, as I have recently found, states in a paper, " Ueber die Leitungsfähigkeit für Elektricität welche Isolatoren durch Temperaturerhöhung annehmen " (*l. c.*), that he has obtained evidence of the electrolytic decomposition of fused mercuric iodide ; and he attributes its apparent conduction without decomposition to recombination of the products. So far as I am aware, no attempt has been made to examine the nature of the conduction of fused mercuric chloride since Faraday concluded that it probably conducted metallically.

Mercuric Iodide.

Mercuric iodide is dimorphic, and at the ordinary temperature forms a scarlet powder which at 110° C. becomes yellow, and at that temperature acquires a very slight electrical conductivity (Beetz). Mercuric iodide melts at 247° C. and boils at 342° C. It is an interesting substance on account of the ease with which it volatilizes at temperatures much below its melting-point ; and it is not unlikely that the ease with which the molecules are thus shown to be leaving the solid substance may be connected with a high diffusive rate when it is fused, and this may partially explain the readiness with which the products of its electrolytic decomposition often mix and recombine, thus simulating conduction without decomposition. The mercuric iodide which I have used in the following experiments was prepared either by the precipitation of recrystallized and sublimed mercuric chloride with pure potassic iodide and sublimation of the product, or by the sublimation of the commercially pure substance.

It may not perhaps be out of place to point out, in the first instance, the effect of heat upon mercuric iodide ; as it is sometimes stated in text-books of Chemistry that, when heated, it undergoes partial dissociation with liberation of iodine, where the edge of the liquid is in contact with the hot glass vessel. I have, however, convinced myself that this statement applies only to the commercially pure substance, which on sublimation leaves a little impure oxide of iron, and which, on the

edges of the glass vessel in which fusion and sublimation are effected, may decompose, yielding free iodine vapour. Pure mercuric iodide may be fused and sublimed without undergoing any such change ; nor have I any reason to believe that, when strongly heated in a sealed glass tube, iodine is ever set free, a slight darkening in the colour of the fused substance being the only apparent alteration which it then undergoes.

Here, too, perhaps it may be convenient to describe the preparation of the graphite electrodes, which for some years past I have found very convenient for the decomposition of such substances as act upon platinum. These electrodes are best made from the " leads " of Rowney's HH cedar pencils, which may be easily removed after a few hours' soaking in water has softened the glue sufficiently to allow of the pencil being split in half. The " lead " is then removed with a knife, and only requires heating to bright redness in a Bunsen-flame (to get rid of the shellac (?) which it contains) to render it fit for use. A platinum wire twisted or bound round one end makes a good connection for the battery-terminals.

When pure mercuric iodide in a sealed glass tube is kept in a state of fusion over a gas-flame, and electrolyzed by means of two platinum-wire electrodes passing through its ends, evidence of its decomposition may be obtained from the iodine set free about the $+$ pole, although no mercury is discoverable at the negative. The quantity of iodine thus set free is, however, small, and does not usually seem to increase with the length of time that the current is allowed to pass ; whilst the decomposition, judging from the liberation of iodine vapour about the positive or upper electrode in the tube, appears to take place at temperatures very little above the solidifying-point of the liquid mercuric iodide.

Electrolysis of this substance kept fused in narrow V- and W-shaped tubes over a gas-flame yields much the same results; but in such tubes the resistance is very high, and it is moreover difficult to ascertain precisely what is taking place within them. I therefore adopted a simple V-shaped glass tube of $\frac{3}{8}$ths of an inch diameter and bent at an angle of about $30°$, into which was placed a sufficient quantity of mercuric iodide for the experiment. The substance was then kept fused over a gas-flame, and the two graphite electrodes introduced, one at each end of the tube. In such a tube the behaviour of the substance is easily observed ; and by blowing air dried over chloride of calcium into the end, the issuing vapours are readily tested for iodine with starch-paper. Under these conditions, I found that when the substance was at a temperature near the melting-point iodine could usually be detected with ease, although at a higher temperature none could be shown to

exist in the free state. A control experiment with fused chloride of lead, using a current of the same strength and the same distance between the electrodes, gave evidence of chlorine without difficulty.

Hence it appeared possible that this substance conducted (as Ag_2S had been supposed to do) in two ways—(α) electrolytically, at a temperature at which it just became liquid; and (β) metallically, at higher temperatures. But during some observations upon the expansion of fused mercuric iodide in a thermometer-like tube, I noticed that the liquid underwent great contraction during cooling from a temperature a little above the melting-point, accompanied by a distinct loss of fluidity. To the latter change I at once attributed the evidence of electrolytic decomposition, which I had observed at a corresponding temperature, to be probably due, as it would be less favourable to the mixing and recombination of the products of electrolytic decomposition; and I therefore turned my attention to the construction of an apparatus in which they should be so separated as to render this less easy.

The form of apparatus which I finally adopted is shown in section in fig. 1. The tube ($a\,b\,c$) containing two small porous battery-pots ($g\,f$), the graphite electrode, and the mercuric iodide to be electrolyzed, is U-shaped, and the two branches are connected by a constricted portion (c), which further materially hinders the mixing of the fused products of decomposition in the two branches of the tube. This apparatus passes through a hole in the tin cover ($j\,i$) which supports it, and dips into the oil in the beaker, which is heated to the desired temperature by means of a gas-flame or sand-bath, at which it is kept constant by placing the bulb of the air-thermometer (h) in communication with a gas-regulator. When mercuric iodide is electrolyzed in such an apparatus with a current of about 0·02 ampere, iodine is liberated at

Fig. 1.

J.W.CLARK DEL

temperatures far above the melting-point of the substance. If the current was too strong the circuit was usually
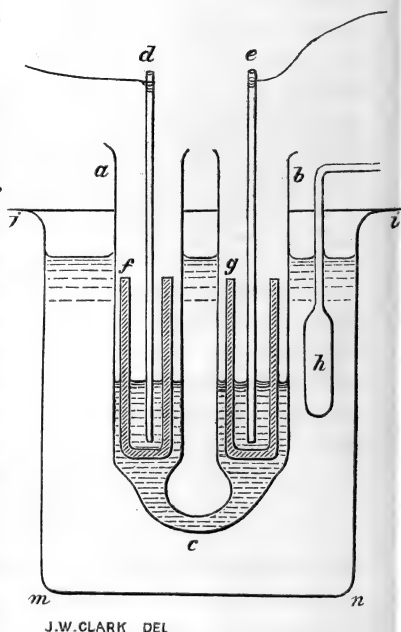
broken, apparently in consequence of the heat generated at the + electrode volatilizing, or otherwise causing the mercuric iodide to disappear from the porous pot. After passing the current for some hours the gas was extinguished, and when the apparatus had become cool the two branches of the U-tube were cut asunder and broken open for examination. In the + branch, both within and without the porous pot, mercuric iodide and black feathery streaks of iodine were found which gave the starch reaction, and the upper part of the glass tube was coated with volatilized iodine.

Iodine dissolves freely in fused mercuric iodide, producing but little change in the colour of the latter ; but just as solidification commences, more or less complete separation seems to take place with the formation of these black patches rich in iodine (and Hg_4I_6?) and an evolution of iodine vapour, which in the previous experiments also helped to lead to the conclusion that electrolytic decomposition occurred only near the melting-point of mercuric iodide.

The contents of the negative branch and porous pot were found to be of a slightly altered colour; but no free mercury was discoverable. Repeated exhaustion of its pulverized contents with absolute alcohol revealed the presence of mercuroso-mercuric iodide (Hg_4I_6 or $2HgI_2$, Hg_2I_2), which might perhaps be inferred to be the first product of the electrolytic decomposition of HgI_2, since it is formed when metallic mercury and mercuric iodide are titurated together in the proper proportions. Mercuroso-mercuric iodide is ordinarily regarded as a distinct compound, and I suppose rightly so ; for it can exist without decomposition at a temperature at which mercurous iodide undergoes decomposition with liberation of free mercury ; but the stability of this body seems to be greatly increased by the presence of a slight excess of mercuric iodide. Mercurous iodide (Hg_2I_2) dissolves readily in fused mercuric iodide in the proportion to form mercuroso-mercuric iodide. The formation of mercuroso-mercuric iodide by the action of the current upon mercuric iodide may therefore be represented by

(i) $2HgI_2 = Hg_2I_2 + I_2,$

(ii) $2HgI_2 + Hg_2I_2 = Hg_4I_6;$
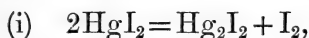
or, considering it to take place in one step,

$$4HgI_2 = Hg_4I_6 + I_2.$$
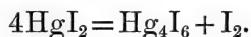
The action being slow I repeated the experiment, replacing the mercuric iodide in the apparatus just described by some mercuroso-mercuric iodide precipitated nearly according to the

equation

$$4KI + I_2 + 2N_2O_4Hg_2O_2 = Hg_4I_6 + 4NO_2KO.$$
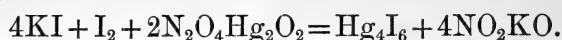
The precipitate was then washed, dried, fused, and finally sublimed from an evaporating dish on a sand-bath into a clock-glass which covered it.   The substance contained a little mercuric iodide as impurity.

The products of the electrolytic decomposition of this substance are mercury and iodine, of which the former is deposited in the metallic condition, apparently according to the equation

$$Hg_4I_6 = 4Hg + 3I_2;$$
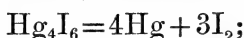
whilst the iodine is absorbed by the Hg_4I_6 in the positive branch of the tube, forming mercuric iodide ; thus,

$$3I_2 + 3Hg_4I_6 = 12HgI_2.$$
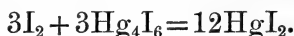
These results may be summarized as follows:—

The conduction of fused mercuric iodide is electrolytic; but decomposition and recombination may take place so rapidly as to give rise to an apparent metallic conduction; but my investigation gives no grounds for supposing that it does not quantitatively conform to Faraday's Laws.

The causes rendering the proof of its electrolytic decomposition difficult may be summed up as follows:—

(1) *Iodine is soluble in fused mercuric iodide, and so is mercurous iodide, in the latter case with the formation of* Hg_4I_6.

(2) *Mercuric iodide is volatile, and the presence of its vapour renders the detection of free iodine difficult by the ordinary test, and also promotes mixture in the electrolytic apparatus by distillation.*

(3) *It also seems possible that fused mercuric iodide possesses a high diffusive rate, which would further facilitate the mixture and recombination of the products of its electrolytic decomposition.*

(4) *The electrical resistance of fused* HgI_2 *is high.*

When pure mercuric iodide is fused over a gas-flame in a straight glass tube, of about 6 centim. in length and 0·5 centim. in breadth, and electrolyzed between platinum wire or graphite electrodes with a current of about 0·20 ampere, the resistance shows some remarkable changes.   Thus:—In an experiment which I copy from my laboratory journal, the resistance of the mercuric iodide in a sealed tube decreased as the temperature rose, until the needle of the tangent-galvanometer which was included in the circuit stood at 20°; and on allowing the temperature to rise still higher, it fell to 9°.   During cooling the inverse change occurred; for on extinguishing the gas and allowing the tube to cool, the needle advanced

from 9° to 20° or 21°, and then fell gradually to 0° as conduction ceased. The cause of this change in the resistance is not very clear. I have assured myself that it is not due to any impurity in the mercuric iodide employed, nor is there a sufficient change in polarization of the electrodes at the different temperatures to account for it. With a very feeble current these resistance-changes are not marked, and indeed may escape observation in an experiment such as that which I have described. I believe this effect to be due, first to the formation, and then to the dissociation or other alteration at the higher temperature of the mercuroso-mercuric iodide produced; in support of which it may be stated that mercurous iodide undergoes rapid decomposition with separation of mercury at about the same temperature at which this change of resistance takes place. Perhaps not entirely unconnected with increase of resistance is the heat generated by the current, in consequence of the transition-resistance at the common surface of the + electrode and fused mercuric iodide, which may occasion the formation of vapour on the surface of the electrode. I have observed this give rise to a crepitating noise, and to the formation of a wave-motion spreading from the + electrode over the surface of the fused substance, and, under favourable circumstances, becoming so marked as to throw the whole tube in which the decomposition was being effected into violent oscillation.

Mercuric Chloride.

Mercuric chloride far exceeds mercuric iodide in the ease with which it volatilizes at temperatures below its melting-point. It melts at 265° C. and boils at 295° C., and is more difficult to decompose with the current than mercuric iodide. This is to some extent due to its higher electrical resistance, which prevents the use of any complex apparatus designed to represent the products of decomposition and prevent their recombination. The mercuric chloride which was used was prepared by the sublimation of the repeatedly recrystallized pure commercial salt.

The apparatus with which I have succeeded in effecting the electrolytic decomposition of fused mercuric chloride is shown in section in fig. 2, and consists of a glass tube of about $\frac{5}{8}$ths of an inch in diameter bent at an angle of 30°. The porous pots (*ab*) and graphite electrodes (*c d*) project at each end, and the requisite temperature was supplied by the hot sand of a sand-bath. With potassic iodide and starch test-paper the evolution of chlorine at the + pole was readily detected, even when a very feeble current was employed. After the current had been passed

through the fused mercuric chloride for some time, the apparatus was allowed to cool, and its contents were subsequently

Fig. 2.

J.W.CLARK DEL
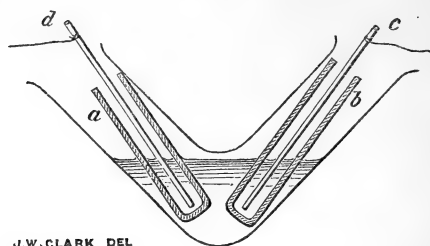
pulverized and exhausted with water, which left an insoluble residue of mercurous chloride (Hg_2Cl_2), which was not entirely confined to the inside of the — porous pot.

Mercurous chloride dissolves in fused mercuric chloride, probably giving rise to a mercuroso-mercuric chloride of analogous composition to some of the well-known double chlorides which mercuric chloride forms. The want of time consequent upon the completion of an investigation on the influence of pressure on electrolytic conduction, upon which I have long been engaged, has prevented my examining this point.

The conduction of mercuric chloride is electrolytic, giving rise to chlorine and mercurous chloride; and there seems no reason to doubt that it conforms quantitatively to Faraday's Law; but the volatility of this substance, as also in the case of mercuric iodide, and of the products of their decomposition, would render its further proof difficult.

The causes rendering its electrolytic decomposition difficult may be summed up as follows :—

(1) *The volatility of mercurous chloride and its solubility in mercuric chloride.*

(2) *The near melting- (265° C.) and boiling- (295° C.) points and great volatility of mercuric chloride facilitate the mixing and recombination of the products of its decomposition, and the vapour renders the detection of chlorine by the ordinary test difficult.*

(3) *As previously stated in reference to mercuric iodide, it is possible that the volatility of these substances is connected with a high diffusive rate, when fused, which would facilitate the recombination of the products of its electrolytic decomposition.*

(4) *The electrical resistance of the fused substance is much higher than that of the mercuric iodide.*

Before concluding this paper, I wish briefly to refer to the properties of fused mercuric iodide and chloride with reference to the porous battery-pots in which the electrodes were

placed, and which seems sufficiently important to merit a few words of description. These porous pots were 2 inches long, $\frac{1}{4}$ inch in diameter, and varied from $\frac{1}{16}$ inch to $\frac{1}{8}$ thick in the walls. My attention was first attracted to their behaviour by noticing that when they were partially dipped into fused mercuric iodide, that liquid rapidly made its appearance in the pot; and the subsequent analysis of the substance surrounding the porous pots after an experiment, showed the presence of small quantities of the products of the decomposition effected by the current, such as iodine, mercuroso-mercuric iodide, and mercurous chloride. Control experiments with water and with fused plumbic chloride showed that these liquids were unable to penetrate the walls of the porous pots.

The explanation of the facility with which fused mercuric iodide penetrates the walls of a porous pot and rises within it seems to be of a complex nature. The imbibition of this fused substance in the porous walls of the pot is due to capillary action, and does not account for the liquid filling the pot; for since it is of a capillary nature, this action must cease as soon as the inner surface or wall becomes wetted. In the case of a volatile liquid such as fused mercuric iodide this action may be somewhat prolonged by its volatilization from the inner surface of the pot-wall, and by the direct formation of crystals from the vapour. The subsequent fusion of these crystals will account for the presence of some liquid mercuric iodide within the porous pot, but then this action must cease. Moreover this explanation apparently requires a difference of temperature within and without the porous pot, which, from some special experiments made upon the subject, can scarcely be assumed to exist; and I therefore think that *the explanation of the penetration of the liquid through the walls of the porous pot must be mainly sought in an easy transpiration of the fused mercuric iodide through its pores in consequence of the small initial difference of level ("head") of the liquid.*

I have already stated that analysis showed the presence of some of the products of decomposition formed within the porous pots in the undecomposed substance in which the latter were partially immersed; and this seems attributable to diffusion through the pot-walls. Little seems known respecting the rates of diffusion of fused substances through porous diaphragms; but the particular difficulties in the way of their determination for such volatile substances (which may so readily mix by distillation) seems of itself suggestive of a molecular activity not unconnected with a long free mean molecular path and of rapid diffusion.

VII. *On the Determination of the Heat-Capacity of a Thermometer.* By J. W. Clark, *Assistant Professor of Physics in University College, Liverpool**.

I. IN the determination of specific heats a correction should be made for that part of the thermometer which is immersed in the water of the calorimeter, as its specific heat is not the same as that of an equal volume of water. Very often this correction is reduced to a mere estimation on account of the unknown weights of glass and mercury which constitute the immersed portion of the thermometer.

When two metals of known specific gravity are fused together, and the volume of the resulting alloy is the sum of the volumes of its two constituents, it is only necessary to know the specific gravity and volume of the piece of alloy to calculate the exact volumes of the metals comprising it. Similarly, by determining the specific gravity and volume of the thermometer, the volume of mercury which it contains can be at once determined from

$$V_1 = \frac{V(S - S_2)}{S_1 - S_2}; \quad \cdots \quad \cdots \quad (1)$$

where V_1 is the required volume of mercury in the thermometer,
V the volume of the thermometer,
S the specific gravity of the thermometer,
S_2 ,, ,, ,, thermometer-glass,
S_1 ,, ,, of Hg.

The mean value of several very closely agreeing determinations of the specific gravity of different specimens of thermometer-glass is $3 \cdot 199$ for lead-glass and $2 \cdot 512$ for soda-glass. Should it not be known of which sort of glass the thermometer consists, it may be readily ascertained by slowly introducing the upper extremity of the instrument into the reducing-flame of a blowpipe :—Soda-glass yields a yellow flame, but lead-glass blackens, from the reduction of the oxide of lead which it contains. It may be assumed that thermometers made on the continent consist of soda-glass ; those made in England are usually constructed of lead-glass.

The total volume of the thermometer (V) is obtained from its weight in air and in water.

The volume of mercury contained in the thermometer having been found by (1), the volume of that part of the thermometer which is immersed in the water of the calorimeter has next to

be determined. This latter volume, less the contained volume of mercury, is the immersed volume of glass.

The total immersed volume (V_3) of the thermometer is best found from the weight (W) of the thermometer in air, and its weight (W_1) when dipped in water to the same depth as it dipped into the water of the calorimeter ; then

$$V_3 = W^{grm.} - W_1^{grm.} \quad . \quad . \quad . \quad . \quad (2)$$

But, if the bulb be cylindrical and of the same diameter as the stem, this volume may be calculated from the measured length and diameter of the immersed portion; for if of an irregular shape it may be found by plunging it into a burette graduated in cubic centimetres and partly filled with water; but in both cases with a less satisfactory result than is given by (2).

The volume of the *glass* of the thermometer (V_2) immersed in the water of the calorimeter is then

$$V_2 = V_3 - V_1.$$

These volumes of glass and mercury are converted into their corresponding weights, using the mean specific gravities of lead- and soda-glass already given. The sum of the products of the weight of the immersed glass and its specific heat, and of the weight of the mercury and its specific heat, is the required water-value of the part of the thermometer dipping into the water in the calorimeter.

Regnault has given the specific heat of thermometer-glass as 0·2; but for greater accuracy it would be desirable that for this value the mean specific heat of lead or of soda thermometer-glass should be substituted according to circumstances [*].

The following is an illustration of the application of the method :—

Thermometer No. 2. *Soda-glass.*

Weight of thermometer in air . . .	= W	33·97 grm.
„ „ water . .		23·01 grm.
Volume of thermometer . . .	= V	10·96 c. c.
Specific gravity of thermometer . .	= S	3·098
Mean sp. gr. of soda-glass	= S_2	2·512
Sp. gr. of Hg	= S_1	13·6

Volume of mercury in thermometer $= V_1 = \dfrac{V(S - S_2)}{S_1 - S_2}$
$= 0·5795$ c.c.

---

[*] It may perhaps be serviceable to call attention to the *Physikalisch-Chemische Tabellen* of Landolt and Börnstein as a work which contains a most useful collection of data.

Weight of thermometer in air . . . . . .   33·97 grm.
Weight of thermometer with lower end immersed in water to the same depth as it was immersed in water of calorimeter $\Bigg\}$ 29·73

Loss of weight=volume of immersed part of thermometer . . . . $\Big\}$ 4·24 c.c.
Subtract contained volume of Hg$=V_1$. $=0·5797$

to get immersed volume of thermometer-glass $=3·661$ c.c.

Weight of this volume of thermometer-glass $3·661 \times 2·512$ . . . .$= \Big\}$ 9·196 grm.
Weight of contained Hg $0·5795 \times 13·6$. $=7·881$

Water-value of immersed glass $9·324 \times 0·2$ $=1·840$
Water-value of immersed Hg $7·881 \times 0·0335 = 0·2639$

Total water-value of the immersed part of the thermometer . . . . $\Big\}$ 2·1039

To test the reliability of the method, I sacrificed the thermometer by cutting off the stem at the level at which it was immersed in the water of the calorimeter, and weighed the quantities of glass and mercury: there were 9·63 and 7·64 grms. respectively, corresponding to a water-value of 2·182, *which ascribes to the above method an error of 3·7 per cent. in the required correction.* This negligible error is due to the volume of the thermometer—consisting, not only of glass and mercury, but also of the unfilled bore of the tube—and to slight deviation of the specific gravity of the thermometer-glass from the mean specific gravity used in the calculation. It may be just worth pointing out that when a fragment of the thermometer-tube is obtained from the maker with the instrument, these errors may be avoided and the *true* water-value obtained. Probably a greater error than the above is introduced into ordinary specific-heat determinations by the evaporation of the water in the calorimeter.

II. A second method for the determination of the water-value of the immersed part of a thermometer may be employed, but it requires that the diameter of the bore of the stem be known. To determine this a fragment of the same thermometer-tube may be obtained from the maker of the instrument, or a short piece of the upper part of the thermometer may be very easily drawn-off before the blowpipe-flame, the closed end of the fragment cut off, and the diameter of the bore measured with a microscope furnished with a micrometer

eye-piece and stage-micrometer. Then the weight of mercury (w), corresponding to an increase of temperature from $0°$ to $100°$ C., is given by

$$w = al \times 13 \cdot 6, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where a is the area of the tube and l the length in centimetres of $100°$ ($t°$) on the scale of the thermometer.

The weight (W) of mercury in the bulb is then

$$W = \frac{w}{\alpha\, t°} + w, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where α is the coefficient of apparent expansion of mercury in glass. For lead-glass $\alpha = 0 \cdot 000155$, and for soda-glass $0 \cdot 0001586$. Having thus determined the quantity of mercury, the quantity of glass may be found as in the first method. With a thermometer containing a known weight of mercury, this method gave a water-value for the immersed part of the instrument which was $3 \cdot 2$ per cent. in error. I place much less reliance upon this than upon the former method, as the apparent coefficient of expansion of glass varies more than its specific gravity. The first method is quick and simple, and the results so excellent, that this second method may be almost regarded as unnecessary; but should any case arise in which it is found to possess advantages over the first, it might be possible to determine the coefficient by observing the increase in length of the thermometer when heated in steam.

University College, Liverpool.

VIII. *On the Error involved in* Professor Quincke's *Method of Calculating Surface-Tensions from the Dimensions of Flat Drops and Bubbles. By* A. M. WORTHINGTON, *M.A., Clifton, Bristol*[*].

IN one of a series of well-known papers (Pogg. *Annal.* vol. cxxxix. part 1 ; and Phil. Mag. April 1871) Prof. Quincke has recorded a large number of measures of flat drops and bubbles, from which he has deduced the value of the tensions, not only at the free surface of liquids, but also at the common surface of two liquids in contact.

The numerical results obtained exceed very appreciably the values of the surface-tensions deduced from observations with capillary tubes, and Prof. Quincke attributes the difference partly to the exposure of the surface of the meniscus in capillary tubes to atmospheric impurities, but chiefly to the fact that with capillary tubes the edge-angle is not zero, and that the quantity measured is not the surface-tension of

* Communicated by the Physical Society : read June 13th, 1885.

the liquid, but the surface-tension multiplied by the cosine of the edge-angle. Thus a special significance has been attached to the high values obtained by the method of flat drops or bubbles, and these values have been widely copied and made the basis of numerical calculations.

The calculation of the results involves the integration of the equation to the liquid surface

$$T\left(\frac{1}{R}+\frac{1}{R'}\right)=Dz.$$

Prof. Quincke starts by writing $\frac{1}{R'}=0$, *i. e.* by assuming that the drop or bubble may be treated not only as flat at the vertex, but also as having an infinite diameter. It is true that in § 5 of the paper referred to he himself comments on the fact that these assumptions are only approximately correct; but he does not attempt to show that the error entailed by these two assumptions is insignificant. It is the object of this paper to show that the error is very considerable, amounting in most cases to as much as 10 per cent. of the whole value, and that when duly corrected the values obtained by this method do not appreciably exceed those obtained with capillary tubes.

Prof. Quincke's process consists in measuring by means of a cathetometer-microscope the dimensions of a large drop or bubble, such as is represented in section in figs. 1 and 2, that has been placed on, or below, a horizontal glass plate.
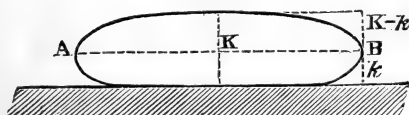
Fig. 1.   Fig. 2.
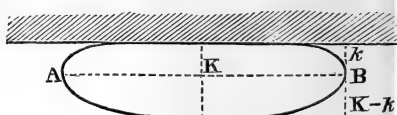
The dimensions measured are

(1) The distance K of the vertex from the plate.
(2) The distance k of the section of maximum radius from the plate.
(3) The maximum diameter AB.

The first two measures afford the value $K-k$ of the distance between the vertex and the section of maximum radius, and the last affords the value L of the maximum radius.

The physical meaning of the assumptions made in the calculation may be explained in the following manner.

Imagine a central slab to be cut out of the drop between two parallel vertical planes at small unit distance apart, and that the slab is again cut in half at right angles to its length,

so that we realize the portion ABCDE′E of the diagram (fig. 3).

Fig. 3.
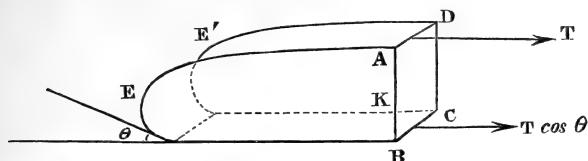
If the drop were of infinite radius, and therefore flat at the top, the slab thus obtained would be equivalent to a similar slab cut out of a mass of liquid, shaped as in fig. 4. If we

Fig. 4.
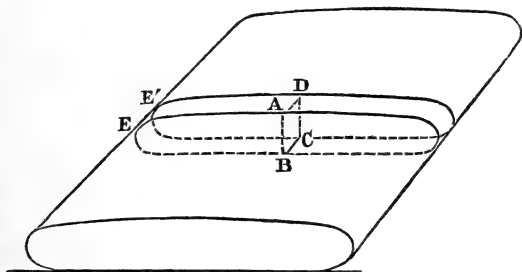
now, on this supposition, consider the equilibrium of the mass represented in fig. 3, with reference to horizontal forces parallel to its length, we can equate the hydrostatic pressure on the rectangular end to the sum of the tensions exerted along the two edges AD and BC. Thus writing, with Quincke, AB=K, and writing D for the difference between the density of the drop or bubble and that of the surrounding medium,

$$T + T \cos \theta = \frac{K^2 D}{2} \; ;$$

whence, when $\theta = 0°$,

$$T = \frac{K^2 D}{4}.$$

Or, if we consider the equilibrium of that portion only of the slab which lies above the horizontal section of greatest area (see fig. 5), we may equate T to the hydrostatic pressure on the rectangular area of unit breadth and depth $(K-k)$,

Fig. 5.
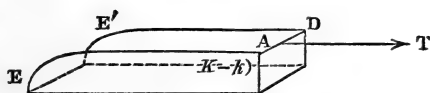
whence

$$T = \frac{(K-k)^2 D}{2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

It is from this equation that Prof. Quincke calculates the value of T.   It is evident that in neglecting the curvature of the vertex we are neglecting the pressure due to this curvature transmitted to the whole area K − k.   Thus, if b be the radius of curvature in question, the pressure disregarded is $\frac{2T}{b}(K - k)$.   The surface-tension T has to balance this as well as the hydrostatic pressure due to the weight of the liquid, and neglect of this term will lead to too small a result.

Again, in neglecting the curvature in the plane at right angles to the plane of the diagram, we evidently leave out of account the tension exerted along each edge AE, DE′, of the slab, which produces a pressure $\frac{T}{R'}$ on each unit area of the surface.

Since the surface is one of revolution, R′ is the length of the normal intercepted by the axis, and writing ϕ for the inclination of the normal to the axis measured on the side of the vertex, *i.e.* for the *edge-angle* of the drop- or bubble-forming fluid at any horizontal section, we have $\frac{1}{R'} = \frac{\sin \phi}{x}$, where x is the horizontal radius of the section ; and the pressure on a horizontal strip of the rectangular end of elementary depth dz is $\frac{T \sin \phi \, dz}{x}$ and the total action omitted,

$$\int_0^{K-k} \frac{T \sin \phi \, dz}{x} ;$$

so that the complete equation is

$$T = \frac{(K - k)^2 D}{2} + \frac{2T}{b}(K - k) - T \int_0^{K-k} \frac{\sin \phi \, dz}{x} \quad . \quad . \quad . \quad (2)$$

The value of the integral of the last term to a first approximation is shown by Laplace (*Méc. Céleste*, livre x. 2ᵉ Suppl. p. 483), or by Mathieu (*Théorie de la Capillarité*, p. 137) to be

$$\frac{4a}{3} \cdot \frac{1 - \cos^3 \frac{\varphi}{2}}{x},$$

where $a = \sqrt{\frac{T}{D}}.$

When x is equal to the maximum radius L, then $\varphi = 90°$, and

the term becomes

$$T \times \frac{4a}{3L} \left(1 - \frac{1}{2\sqrt{2}}\right).$$

We may use for (a) in this corrective term the value given by the approximate equation (1),

$$T = \frac{(K-k)^2 D}{2} ;$$

whence

$$\sqrt{\frac{T}{D}} = a = \frac{K-k}{\sqrt{2}}.$$

Thus the term in question reduces to

$$2T \frac{K-k}{3 \cdot 282 L} ;$$

and the complete equation (2) becomes

$$T = \frac{(K-k)^2}{2} D + \frac{2T}{b}(K-k) - \frac{2T(K-k)}{3 \cdot 282 L} ;$$

or

$$\frac{T}{D} = \frac{(K-k)^2}{2} + \frac{T}{D} 2(K-k)\left(\frac{1}{b} - \frac{1}{3 \cdot 282 L}\right).$$

Or, writing $-C$ for the value of the factor $\left(\frac{1}{b} - \frac{1}{3 \cdot 282\, L}\right)$ in the corrective term,

$$\frac{T}{D} = \frac{(K-k)^2}{2(1 + 2\overline{K-k}C)}. \quad . \quad . \quad . \quad (3)$$

To find the value of C we must know that of $\frac{1}{b}$. This is shown by Laplace (*loc. cit.* p. 485) or Mathieu (*loc. cit.* p. 140) to be equal to

$$2\sqrt{2}a^{-\frac{3}{2}}\sqrt{\pi x} \tan \frac{\phi}{4} e^{-\frac{x}{a} - 4\sin^2\frac{\phi}{4}} ;$$

which, when $x = L$ and $\phi = 90°$, reduces to

$$\frac{1}{b} = \sqrt{\frac{8\pi L}{a^3}} \times \cdot 4142136 \times e^{-\frac{L}{a} + \cdot 585788},$$

in which we may use for a the mean value of $\frac{K-k}{\sqrt{2}}$ found by Prof. Quincke.

Before giving the numerical results, it is necessary to

observe that the value of the integral $\displaystyle\int_{z=0}^{z=K-k} \frac{\sin\phi\, dz}{x}$ is calculated

on the assumption that the fraction $\dfrac{a}{L}$ is small; and, again, the value of $\dfrac{1}{b}$ is calculated on the assumption that $\dfrac{dz}{dx}$ is small, even when x is large, *i. e.* that the drop is very flat, even far from the vertex. Now the drop or bubble used by Prof. Quincke was often far from satisfying these conditions. In some cases the diameter was so small that the fraction $\dfrac{a}{L}$ amounted to as much as $\frac{1}{2}$, and the curvature at the vertex was so considerable that the value of $\dfrac{1}{b}$ cannot be satisfactorily calculated in the way described. Thus in the first measure of an air-bubble in water (Quincke, *loc. cit.* § 3, table III.) $\dfrac{a}{L} = \cdot319$; while in the case of drops of petroleum in water it is as much as $\cdot3768$.

I have therefore selected for correction only those measures for which the value of $\dfrac{a}{L}$ was smallest, though the mean value of the observed quantity $K-k$ used in calculating $\dfrac{1}{b}$ was generally taken from the whole of the measures given by Prof. Quincke.

<div align="center">

Air-bubbles in Hyposulphite of Soda.

$D = 1\cdot1248.$

</div>

No.	L.	$K-k$.	$\dfrac{1}{3\cdot282\,L}$	$\dfrac{1}{b}$	Grams per cm.	
					S. tension (Quincke).	S. tension, corrected.
3.	1·41	·3738	·2161	·0492	·07856	·06853
4.	,,	·3662			·07541	
	Mean (of 4 measures)				·07903	
	By capillary tubes (Quincke)				·07636	

(The mean of $K-k$ used to calculate $\dfrac{1}{b}$ was $\cdot37485$.)

Air-bubbles in Distilled Water.

D=1.   Temp. 25° C.

No.	L.	$K-k$.	$\dfrac{1}{3 \cdot 282\,L}$	$\dfrac{1}{b}$	Grams per cm.		
					S. tension (Quincke).	S. tension, corrected.	
1.	·9	·4112	·3385	·3104	·08455	·08263	Rejected.
2.	1·38	·4069	·2208	·0723	·08280	·07386	
3.	1·05	·3972	·2902	·1989	·07905	·07355	
4.	1·095	·4043	·2783	·1736	·08170	·07535	
5.	1·00	·4011	·3047	·2310	·08040	·07595	
6.	1·04	·4225	·2930	·2049	·08920	·08307	
7.	1·535	·4000	·1985	·0443	·08000	·07122	

Mean (of 7) .... ·08253   ·07550

By capillary tubes (Quincke) ...   .   ·07235 at temp. 16°·2.

If we reject also Nos. (3), (5), and (6) on account of the largeness of the fraction $\dfrac{a}{L}$, the mean result is...   ·07348

The exps. of M. Wolf (see Terquem's *Capillarité*, p. 34) give .... ·07345 at temp. 25° C.

Air-bubbles in Bisulphide of Carbon.

D=1·2687.   Temp. 25° C.

No.	L.	$K-k$.	$\dfrac{1}{3 \cdot 282\,L}$	$\dfrac{1}{b}$	Grams per cm.	
					S. tension (Quincke).	S. tension, corrected.
1.	1·25	·2180	·2438	·0093	·03015	·027351
2.	1·35	·2230	·2226	·0046	·03157	·0287
3	1·75	·2399	·1741	0	·03651	·03369

Mean .... ·03274   ·0299

By capillary tubes (temp. 18°) (Quincke) ...   .   ·03343

Air-bubbles in Olive-oil.

D = ·9136.   Temp. 25°·8 C.

No.	L.	K−k.	$\dfrac{1}{3\cdot282\,L}$	$\dfrac{1}{b}$	Grams per cm.	
					S. tension (Quincke).	S. tension, corrected.
	cm.	cm.				
1.	1·5	·3001	·2031	·0095	·04113	·03678
2.	1·7	·2858	·1792	·00377	·03735	·03387
3.	1·7	·2885	,,	,,	·03804	·03453
4.	1·56	·2905	·1953	·00719	·03850	·03470
5.	1·56	·2814	,,	,,	·03617	·03271
6.	1·485	·2751	·2052	·01041	·03457	·03122
7.	1·485	·2861	,,	,,	·03741	·03364
Mean					·03760	·03392
By capillary tubes (temp. 22°) (Quincke).					......	·03271

Air-bubbles in Oil of Turpentine.

D = ·8867.   Temp. 25°·1 C.

No.	L.	K−k.	$\dfrac{1}{3\cdot282\,L}$	$\dfrac{1}{b}$	Grams per cm.	
					S. tension (Quincke).	S. tension, corrected.
	cm.	cm.				
3.	1·34	·2665	·2274	·01199	·03149	·02818
4.	,,	·2659			·03134	
Mean (of 8 measures)					·03033	·02818
By capillary tubes (temp. 21°·7) (Quincke) .					......	·02765

(The mean value of K−k used in the calculation of $\dfrac{1}{b}$ is ·2615 cm.)

Air-bubbles in Petroleum.

D=0·7977. Temp. 24°·2 C.

No.	L.	K−k.	$\dfrac{1}{3\cdot282\,L}$	$\dfrac{1}{b}$	Grams per cm.	
					S. tension (Quincke).	S. tension, corrected.
1.	cm. 1·475	cm. ·2838	·2066	·01033	·03212	·02890
2.	1·5	·2860	} ·2031	·0090	·03260	·02934
3.	,,	·2858				
Mean (of 3 measures)					·03244	·02912
By capillary tubes (temp. 22°·3)...............					......	·02566

Air-bubbles in Absolute Alcohol.

D=·7906. Temp. 25°·3 C.

No.	L.	K−k.	$\dfrac{1}{3\cdot282\,L}$	$\dfrac{1}{b}$	Grams per cm.	
					S. tension (Quincke).	S. tension, corrected.
1.	cm. 1·57	cm. ·2532	} ·1959	·00326	{ ·02533	} ·02335
2.	,,	·2560			·02591	
3.	1·415	·2611	} ·2153	·0074	{ ·02695	} ·02417
4.	,,	·2548			·02566	
5.	1·41	·2539	} ,,	,,	{ ·02548	} ·02324
6.	,,	·2560			·02590	
7.	1·44	·2573	} ·2116	·0063	{ ·02616	} ·02383
8.	,,	·2591			·02655	
					·02599	·02367
By capillary tubes at 21°·8 (Quincke)					......	·02237
,, ,, ,, ,, 15° (Mendeléeff)					......	·02365

Mercury in Air.
D=13·5432.   Temp. 20° C.

No.	L.	K−k.	$\dfrac{1}{3\cdot282}$ L.	$\dfrac{1}{b}$.	Grams per cm.	
					S. tension (Quincke).	S. tension, corrected.
6.	1·625	·2839	·1875	·00534	·5456	·4946
7.	1·7	·2861	·1792	·00377	·5546	·5037
8.	1·65	·2822	(C calculated by proportional parts.)		·5624	·5102
			Mean of 8 measures ...		·5503	·5028

(The mean of K−k used to calculate $\dfrac{1}{b}$ was ·2863.)

Bisulphide of Carbon in Water.
D=1·2687−1.

No.	L.	K−k.	$\dfrac{1}{3\cdot282}$ L.	$\dfrac{1}{b}$.	Grams per cm.	
					S. tension (Quincke).	S. tension, corrected.
1.	1·275	·5510			·04069	
2.	,,	·5478	·2389	·2082	·04021	·03872
3.	,,	·5390			·03893	
4.	1·355	·5830	·2249	·1753	·04555	·04301
5.	,,	·5808			·04520	
			Mean of 6 measures ...		·04256	·04086

(The mean of K−k used to calculate $\dfrac{1}{b}$ was ·5583.)

Chloroform in Water.
D=0·4878.

No.	L.	K−k.	$\dfrac{1}{3\cdot282}$ L.	$\dfrac{1}{b}$.	Grams per cm.	
					S. tension (Quincke).	S. tension, corrected.
4.	cm. 1·8	cm. ·3450	·1693	·0089	·02902	·026296
5.	,,	·3472			·02941	
			Mean of 5 measures ...		·03010	

(The mean of K−k used to calculate $\dfrac{1}{b}$ was ·35076.)

Olive-oil in Water.
$D = 1 - 0.9136.$

No.	L.	$K-k$.	$\dfrac{1}{3.282\,L}.$	$\dfrac{1}{b}.$	Grams per cm.	
					S. tension (Quincke).	S. tension, corrected.
6.	cm. 2·37	cm. ·6941	} ·1286	} ·04185	·02082	} ·01818
7.	,,	·6785			·01988	
			Mean of 7 measures ...		·02096	

(The mean of $K-k$ used to calculate $\dfrac{1}{b}$ was ·69648.)

Turpentine in Water.
$D = 1 - 0.8867.$

No.	L.	$K-k$.	$\dfrac{1}{3.282\,L}.$	$\dfrac{1}{b}.$	Grams per cm.	
					S. tension (Quincke).	S. tension, corrected.
9.	cm. 1·15	cm. ·4610	·2649	·1915	·01200	·01127
			Mean of 9 measures ...		·01177	

(The mean of $K-k$ used to calculate $\dfrac{1}{b}$ was ·4562.)

Mercury in Aqueous Solution of Hyposulphite of Soda.
$D = 13.543 - 1.1248.$

No.	L.	$K-k$.	$\dfrac{1}{3.282\,L}.$	$\dfrac{1}{b}.$	Grams per cm.	
					S. tension (Quincke).	S. tension, corrected.
4.	cm. 1·365	cm. ·2836	}	}	·4994	}
5.	,,	·2730	·2232	·01405	·4628	·4208
6.	,,	·2680			·4459	
			Mean of 6 measures ...		·45107	

(The mean of $K-k$ used to calculate $\dfrac{1}{b}$ was ·2749.)

Mercury in Water.

$$D = 13.543 - 1.$$

No.	L.	K−k.	$\dfrac{1}{3.282\,L}$	$\dfrac{1}{b}$	Grams per cm.	
					S. tension (Quincke).	S. tension, corrected.
	cm.	cm.				
3.	1·5	·2560			·4110	
4.	,,	·2605	·20313	·00514	·4256	·3844
5.	,,	·2607			·4262	
7.	,,	·2527			·4005	
			Mean of 7 measures ...		·4258	

(The mean of K−k used to calculate $\dfrac{1}{b}$ was ·26.)

Mercury in Olive-oil.

$$D = 13.543 - 0.9136.$$

No.	L.	K−k.	$\dfrac{1}{3.282\,L}$	$\dfrac{1}{b}$	Grams per cm.	
					S. tension (Quincke).	S. tension, corrected.
	cm.	cm.				
3.	1·45	·2362			·3523	
4.	,,	·2282	·21014	·00306	·3288	·31066
			Mean of 6 measures ...		·3419	

(The mean of K−k used to calculate $\dfrac{1}{b}$ was ·2322.)

Mercury in Oil of Turpentine.

$$D = 13 \cdot 543 - 0 \cdot 8867.$$

No.	L.	K−k.	$\dfrac{1}{3 \cdot 282\,\mathrm{L}}$	$\dfrac{1}{b}$	Grams per cm.	
					S. tension (Quincke).	S. tension, corrected.
1.	cm. 1·5	cm. ·1967			·2449	
2.	,,	·2054	·20313	·0007	·2669	·2415
3.	,,	·2044			·2642	
4.	1·815	·1970	·20313	0	·2456	·2304
				Mean ...	·2554	·236

(The mean of K−k used to calculate $\dfrac{1}{b}$ was ·2009.)

Mercury in Petroleum.

$$D = 13 \cdot 543 - 0 \cdot 7977.$$

No.	L.	K−k.	$\dfrac{1}{3 \cdot 282\,\mathrm{L}}$	$\dfrac{1}{b}$	Grams per cm.	
					S. tension (Quincke).	S. tension, corrected.
3.	cm. 1·9	cm. ·2010	·1604	0	·2574	·23896
4.	,,	·1985			·2511	
5.	1·5	·2220	·20313	·0022	·3142	·29171
6.	,,	·2247			·3218	
				Mean ...	·2861	·2653

(The mean of K−k used to calculate $\dfrac{1}{b}$ was ·21155.)

Mercury in Alcohol.

$$D = 13 \cdot 543 - 0 \cdot 7906.$$

No.	L.	K−k.	$\dfrac{1}{3 \cdot 282\,L}$.	$\dfrac{1}{b}$.	Grams per cm.	
					S. tension (Quincke).	S. tension, corrected.
	cm.	cm.				
1.	1·5	·2443			·3805	
2.	,,	·2574	·20313	·0037	·4224	·3569
3.	,,	·2422			·3740	
		Mean of 6 measures ...			·4025	

(The mean of K−k used to calculate $\frac{1}{b}$ was ·248.)

Olive-oil in Alcohol.

$$D = \cdot 9136 - \cdot 7906.$$

No.	L.	K−k.	$\dfrac{1}{3 \cdot 282\,L}$.	$\dfrac{1}{b}$.	Grams per cm.	
					S. tension (Quincke).	S. tension, corrected.
3.	1·405	·1975			·00240	
4.	,,	·1872	·21686	0	·00215	·00210
		Mean of 4 measures...			... .. ·00226	

(The mean of K − k used to calculate $\frac{1}{b}$ was ·1917.)

The corrected results with hyposulphite of soda, bisulphide of carbon, and petroleum do not agree satisfactorily with the measures made with capillary tubes.

The general effect of the correction is to reduce the results by about 10 per cent., but in some cases, especially of drops of one liquid in another, the value of L is so small that the accuracy of the correction may be questioned. I hope soon to be able to lay before the Society fresh determinations of the surface-tension in these cases. When L reaches or

approaches 2 centims. the term $\frac{1}{b}$ is generally insignificant, though the corrective factor C, which now reduces to $\frac{1}{3 \cdot 282 \, L}$, is still important. In fact a drop or bubble may be considered flat before the radius can be regarded as indefinitely great.

In those cases where the corrected value still exceeds the mean value obtained by the method of capillary tubes, the difference which was previously considerable is now for the most part insignificant ; witness water, olive-oil, turpentine, and alcohol. It must also be remarked that the measures of flat drops or bubbles agree among themselves far less satisfactorily than the measures of capillary elevations. Thus the numbers quoted as obtained with capillary tubes are themselves the mean of several observations, not differing from each other as a rule by more than 2 per cent., though made with tubes of various diameters; while the observations of flat drops or bubbles differ often by as much as 15 per cent., or even more.

This very variation is indeed a matter of interest, and not easily accounted for[*]. For though M. van der Mensbrügghe has well pointed out [†] that the bubble when first blown must exhibit a higher surface-tension, owing to the absorption of heat from, and consequent lowering of temperature of, the surface-layers, yet it is not easy to believe that this deviation from the normal value would be of long persistence ; nor indeed do Prof. Quincke's measures always show a diminution of tension with the time.

I think, however, that we may draw the conclusion that the method of capillary tubes, when care is taken thoroughly to wet the walls above the meniscus, leads to values which are not discredited, as we had been led to think, by the results of the method of flat drops or bubbles. This is a satisfactory conclusion to come to, since the method of elevation in capillary tubes is that which has been most frequently employed for measuring the surface-tension. Prof. Quincke's value ($\cdot 0825$ gr. $= 81$ C.G.S. units) of the surface-tension of water

---

[*] Mr. Bashforth (see 'An Attempt to test the Theories of Capillary Action,' p. 10) remarks on the difficulty of making any accurate direct measurement of the height $K - k$, and Prof. Guthrie has somewhere noticed the same difficulty. But Prof. Quincke's measures of $K - k$ do not show a percentage-variation much greater than that of the quantity $K \sqrt{\frac{1}{2}}$, in determining which the same difficulties do not occur.

[†] " Etudes sur les variations d'énergie potentielle des surfaces liquides," *Mém. de l'Acad. de Belgique*, t. xliii. 1878.

has been employed by Lord Rayleigh * to calculate the wave-length in an oscillating water-jet, and leads, as he himself points out, to too low a result. Had he made use of the corrected value (T= ·0735 gr.= 72·1 C.G.S. units), the results of p. 82, *loc. cit.*, would have been in very close agreement with theory.

In conclusion, I would remark that the great value of this particular paper of Prof. Quincke's does not, as it seems to me, depend so much on the absolute accuracy of the results presented as on the emphasis with which, at the time it was written, it represented the capillary constant to be measured as a surface-tension, and on the justice of the general considerations which are put forward, and which remain unimpeached.

<div style="text-align: right">A. M. WORTHINGTON.</div>

Clifton, Bristol, June 2, 1885.

P.S. For the benefit of readers of Maxwell's 'Theory of Heat,' in which Prof. Quincke's results are given in a synoptic table, I here reproduce the table with the corrected values. Those in brackets I have been unable to check. It must be borne in mind that the numbers in the second column of tensions are still somewhat uncertain.

The values are given in grammes weight per linear metre.

Superficial Tensions at about 20° C.

Liquid.	Specific gravity.	Tension separating the liquid from		
		Air.	Water.	Mercury.
Water..........................	1·0	7·35	0	38·44
Mercury.......................	13·543	50·28	38·44	0
Bisulphide of Carbon	1·2687	2·99	4·09	[37·97]
Chloroform	1·4878	[3·12]	2·63	[40·71]
Alcohol	0·7906	[2·36]	...	35·69
Olive-oil......................	0·9136	3·39	1·82	31·07
Turpentine	0·8867	2·82	1·13	23·60
Petroleum	0·7977	2·91	[2·83]	26·53
Hydrochloric acid	1·1	[7·15]	...	[38·41]
Solution of Hyposulphite of Soda	1·1248	0·85	...	42·08

---

* "On the Capillary Phenomena of Jets," Proc. Roy. Soc. no. 196 (1879).

IX. *The Stream-lines of Moving Vortex-rings.*   *By* OLIVER
   LODGE *D.Sc., Professor of Physics in University College,
   Liverpool**.
[Plates II., III., IV.]

THE object of the present communication is to publish
   drawings of vortex stream-lines, some of which I made
originally for my own edification.   Taking the lines of a
stationary vortex, as given by Sir W. Thomson in his memoir
on Vortex Motion (Trans. Roy. Soc. Edinb. vol. xxv.), or as
copied into Maxwell's 'Electricity' (plate 18, vol. ii.), I merely
superpose uniform motion upon them, in the shape of a series
of parallel lines, and join up the corners of the quadrangles
so formed.

   Another way of expressing the matter is to say that you
draw the lines of magnetic induction due to a circular ring
conveying a current, placed in a uniform magnetic field with
its lines exactly opposed to those inside the ring.

   I choose two strengths of uniform field for the sake of
illustration; one distinctly stronger, the other distinctly weaker,
than the central intensity due to the coil alone.   The relative
intensities at centre of ring due to field and coil respectively
are about as 1 to 5 in fig. 1, and as 64 to 5 in fig. 2 (Plate II.).
Or, taking the curves as representing stream-lines: in fig. 1
the velocity of vortex-motion is equal to the translation-
velocity of the whole ring at a certain circle in its plane
concentric with its core and of 3·3 times the diameter of the
core, and also at two points on the axis; while in fig. 2 the
vortex-velocity and the translation-velocity are equal at a place
1·5 core-radii distant from the centre of the ring outside, and
at another circle, say two fifths the core dimensions, inside,
the ring.

   In fig. 1 the ring is moving so fast that the translational
flow back of fluid through its centre overpowers the forward
vortex-motion there.   In fig. 2 the vortex-motion predo-
minates as far as a point on the axis which I reckon as 1·38
core-radii distant from centre of ring, a point indicated by the
crossing of the partially dotted stream-line.   It will be under-
stood that though they look so different, the two Plates repre-
sent the *same* ring moving at different speeds. The size of
the core or circular axis is the same in both diagrams.

   It will be observed that in fig. 2 the portion of fluid
permanently partitioned off from the rest by reason of its
vorticity is truly ring-shaped, and would become thinner or
more wiry if its forward motion were greater—the lines near
the core of the ring being prolate towards the axis; while
in fig. 1 the rotational portion of fluid, which is being bodily

* Communicated by the Physical Society : read June 27, 1885.

translated through the rest, forms an ovoid mass with dimples before and behind—the dimples, however, becoming less and disappearing when the translatory motion is made still slower. The lines near the core are in this case rather displaced away from the axis.   The dottedness of the portion of the line which crosses the axis of the ring is purely subjective, and only indicates uncertainty on my part as to its exact course, from want of knowledge.   It is probable that the same defect exhibits itself in my terminology, which is probably incorrect, or at least unusual.   Thus I cannot help calling the actual circular axis of the ring its "core," instead of the whole of the rotational portion, as is usual in dealing with rings of very small cross section in proportion to area of ring itself.   The rings drawn are not of small cross section, and so one wants a name for their innermost axis or core.

We can try to apply Sir William Thomson's rule[*] for the velocity of translation of very thin or high-speed rings, to the case of fig. 2 ; though this ring is not nearly thin enough for the formula to be properly applicable.

Using the symbol λ for the ratio of radius of ring itself to its cross-section radius, the rule may be written:—

$$\frac{2\pi \times \text{velocity of translation}}{\text{vortex velocity at centre of ring}}$$
$$= \frac{2\lambda \times \text{velocity of translation}}{\text{vortex velocity at surface of rotational portion}} = \log\left(8\lambda - \tfrac{1}{4}\right).$$

In fig. 2 the value of λ is about 3 ; and accordingly each of the above terms is about 3 also; or the two vortex velocities specified in the formula are nearly equal, and about double that of the translational velocity.

This does not agree with what I said before, about the ratio of uniform field to ring-field at centre being as 64 : 5 ; hence there is something wrong, but I don't know what.   The lines of uniform velocity in fig. 2 were taken 8 times as close together as in fig. 1; and this surely represents a velocity 64 times as great.   I can only suppose that the ring is *much* too fat for the formula.

Plate III. is an attempt to represent a vortex-ring advancing in a very imperfect or viscous fluid, showing its gradual increase in size, and decrease in forward velocity.   It is easily drawn by superposing a diverging equiangular pencil on the stationary vortex which forms the basis of all three diagrams ; but that it really represents the effect of viscosity does not seem very probable.   No *slip*, due to inertia of displaced fluid, is shown in any of the diagrams.   This figure better represents a ring moving towards a large distant obstacle.   As

* Phil. Mag. June 1867, xxxiii. p. 511.

drawn, the vortex-velocity at centre is only a trifle greater than the translational velocity. This plate also represents the lines of magnetic force due to a circular current with a repellent pole on its axis, at a point 2·518 diameters away from the plane of the circle. The dots on the curves indicate the distribution of the crossing-points which guide the drawing.

Plate IV. shows the attempt of a ring to advance in an oblique direction, not normal to its plane. It is supposed to have been knocked out of a hole by a slant impulse. There is evidently a good deal of vibration, both of the ring as a whole and of its cross section; and it looks as though a very little would suffice to break it up altogether. The resultant velocity at the centre of the ring happens, in the particular case here chosen, to be about zero.

In cases of oblique progression a tendency to a bodily shifting of the uniform flow-lines, parallel to themselves, as they pass from before to behind the ring, is noticeable, and is exhibited in fig. 1. Perhaps this means a heaving or sinuous path of motion for the ring. The right mode of joining up the guiding-points is however in this case by no means obvious; and fig. 2 (Plate IV.) is just as likely to be correct as fig. 1. In fig. 2 no shifting of distant stream-lines occurs, but then it hardly seems a real case of vortex-motion: at least it looks only like a ring shaking itself to pieces; while fig. 1 suggests an attempt of the same ring to pull itself together.

I have a number of other diagrams drawn in the rough, indicating various features of the clash or chase of vortex-rings.

The direct clash of two equal opposite rings, or the impact of one against a looking-glass, is of course very easy. The clash of two rings of different strength is more complex—one appears to be opened out over the other.

The chase of two unequal rings, and the penetration of the front one by its pursuer, are well shown; but if the rings are of equal strength they refuse to penetrate, and seem to amalgamate or pair, no matter at what different speeds they may be going.

The deflection of one ring by another whose path is inclined to it, as calculated by Prof. J. J. Thomson in his 'Adams Essay,' * can also be illustrated, together with what I think corresponds to vibrations of the core about the circular form.

But all these diagrams I propose to publish in a more complete form later. This "experimental" method of investigation, by diagrams based on simple superposition of velocities, seems capable of great extension, because one is limited by no approximations or conditions: the only difficulty is the interpretation of results.

* See also Phil. Trans. ii. 1882.

Last year I examined air vortex-rings produced in the well-known manner described by Prof. Tait[*], in the light of a powerful intermittent induction-coil Leyden-jar discharge. The motion is, however, of too continuous a nature to exhibit the advantages of this mode of illumination ; and though the crispations of vibrating rings are well shown, there is no obvious peculiarity noticeable which does not show itself equally well in a steady illumination.

This paper is only to be regarded as a preliminary note, and, as Prof. Carey Foster has kindly reminded me, the uniform field as I have drawn it is not quite correct. This indeed will account for the discrepancy between theory and experiment mentioned above.

The appearance of jets of water illuminated intermittently is, as is well known, very striking; and I have long imagined that a waterfall illuminated in this way would be a striking spectacle. The spark is scarcely bright enough for large-scale illumination, though there is nothing to beat it for instantaneousness. A revolving slit-disk would, however, prove a more manageable and less noisy method, and by a judicious arrangement of special lenses it can be made to give plenty of light. But the speed of the disk must be high, and its slits narrow, or the drops will be blurred and their characteristic statical beauty lost.

X. *Notices respecting New Books.*

Geschichte der Elektrizität. *Von* Dr. Edm. Hoppe.
Leipzig: J. A. Barth (pp. 620).

THE work before us may be characterized as encyclopædic. It is one of those valuable contributions to scientific literature of which we owe so many to the laborious research of our German friends, but which, for some reason, are found in English, for the most part, only in the form of translations. But Dr. Hoppe's book is not only a valuable collection and *résumé* of all that has been done in Electricity from the earliest times down to the present date, but it is also a veritable romance, in which the story of discovery in this particular science is told in a most fascinating manner. We are nowadays so familiar with the achievements of science, and so accustomed to see the giant of Electricity tamed and made to serve the purposes of every-day life, that we are apt to overlook the difficulties with which the earlier investigators had to contend ; and it is just here that the charm of such a history as the one before us lies,—that, being familiar with the results of which the original discoverers were in search, we are able to survey their labours, to trace where, having hit upon the right track, they have pursued the truth, till their labours have been crowned with success, and to admire the skill with which they have overcome the difficulties in their way.

[*] ' Recent Advances, p. 292.

Dr. Hoppe divides his work into six Books, which deal with different epochs in the history of Electricity, and which are, of course, of very unequal bulk. The first gives us the history of discovery from the earliest times to Franklin, and occupies 28 pages. The second embraces the times of Franklin and Coulomb, 1747 to 1789, 70 pages. Book III. gives us the history from Galvani's discovery to the year 1819, treating chiefly of galvanic electricity and the discoveries of Volta, Davy, Oerstedt, Zamboni, and others, occupying 73 pages. Book IV. treats of the connection between Electricity and Magnetism, and of the contributions to electrical science of Oerstedt, Poggendorff, Schweigger, Ampère, Faraday, and Nobili, in the years 1820–26, and covers 60 pages. Book V. extends from Ohm to the recognition of the law of conservation of energy (1827–47, 260 pages), including, amongst others, the researches of Ohm, Pouillet, Kohlrausch, Faraday, Schönbein, Daniell, Grove, Bunsen, Poggendorff, Planté, Faure, Joule, Lenz, Peltier, Kirchhoff, Gauss, Wheatstone, Weber; and Book VI. treats of the technical applications of Electricity—of the electric light, dynamo machines, the electric telegraph, and telephone, &c.: this occupies 93 pages.

It is not practicable, within the limits of a brief notice, to do more than mention one or two points which may be of interest. Dr. Hoppe discusses the question of the discovery of the Leyden jar at some length, and, apparently, gives his verdict in favour of Kleist as the actual discoverer; at least he seems to adopt the name "Kleist's jar" instead of the usual term. Von Kleist, Bishop of Kammin, in Pomerania, on the 11th October, 1745, placed a nail in a medicine-glass and held it to the conductor of an electrical machine; on touching the nail with the other hand he received a shock, especially if the glass contained mercury; and this appears to be the first time the experiment was ever made. This result was communicated by letter to at least three people, in Berlin, Halle, and Danzig respectively, in November and December of the same year.

In January 1746 a similar observation was made, accidentally, by Cunæus, in Leyden, and repeated by Musschenbroek, Professor of Mathematics and Physics at the University of Leyden, and Gallamand, Professor of Philosophy at Leyden, who communicated the discovery to the famous Abbé Nollet, in Paris, who, knowing nothing of Von Kleist, accredited the discovery to the Leyden professors. It would appear, then, to be due to the accident of the general ignorance of the German language, in comparison to the widespread use of the French tongue, that this most important discovery has been connected with Leyden and not with the name of Von Kleist; and there is some foundation for Dr. Hoppe's complaint, that whereas every schoolboy knows what a Leyden jar means, perhaps not one ever heard the name of Von Kleist.

Some of our common appliances or observations seem to date back further than is usually supposed. We note that the date of the first lightning-rod is given by Dr. Hoppe as 1754, and that

it was erected by Procopius Divisch, although the suggestion was made by Franklin in 1749. The first observation of chemical decomposition by means of the galvanic current is ascribed to Dr. Asch, of Oxford, in 1795. Humboldt, repeating the experiment, first collected hydrogen from the galvanic decomposition of water; and Nicholson, in 1800, making the necessary substitution of platinum electrodes for those of brass or copper, first collected oxygen from this source. The first electro-plating was effected by Ritter in 1800, who deposited copper by means of the galvanic current. The first construction of a secondary battery is assigned to Gautherot, in 1802; and the first construction of a dry pile, with which the name of Zamboni is usually associated, is shown to rest with Behrens, who constructed such a pile in 1803, seven years earlier than Zamboni.

Respecting the rediscovery of Ohm's Law by Pouillet, Dr. Hoppe writes :—" Pouillet does not say whether or not he was previously acquainted with Ohm's law; the attempt has since been made to claim the priority of the discovery for Pouillet, which is the more absurd since it has not yet been determined that Pouillet was not acquainted with the researches of Ohm and Fechner. For, as I have already had occasion to remark, when Englishmen or Frenchmen do not cite a German work, that is no reason for supposing that they are not acquainted with it. Since Pouillet had been for a long time in scientific correspondence with Poggendorff, as, indeed, appears from the abstracts of his work, which he himself prepared for Poggendorff's *Annalen*, it appears to me very probable that Pouillet was acquainted with Ohm's work, and that his excellent experiments therefore, as, indeed, Poggendorff remarks in a note, were only a confirmation of Ohm's theory."

The fifth and sixth books, which, of course, occupy the most space, are particularly full and interesting, but space forbids detailed reference. We merely mention the account given of the introduction of the idea of "potential" into electrical theory, and the history of the various forms of incandescent lamp. Dr. Hoppe does not seem disposed to credit Edison with quite so much originality as he is generally supposed to have.

Dr. Hoppe has produced a most valuable and interesting work, which will be cordially welcomed by those interested in the subject who are acquainted with the German language. It is to be hoped that an English version may be produced.

XI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

May 13, 1885.—Prof. T. G. Bonney, D.Sc., LL.D., F.R.S., President, in the Chair.

THE following communications were read :—

1. "On the Ostracoda of the Purbeck Formation; with Notes on the Wealden Species." By Prof. T. Rupert Jones, F.R.S., F.G.S.

2. "Evidence of the Action of Land-ice at Great Crosby, Lanca-shire." By T. Mellard Reade, Esq., F.R.S.

The Author pointed out that the Triassic rocks under the Low-level Boulder-clay in the neighbourhood of Liverpool, where they are not smoothed and striated, are usually broken up into rubble and red sand, forming a bed of variable thickness occasionally consolidated into a breccia. This deposit he had in former papers attributed to the action of land-ice. At Mowbrey brick-and-tile works, Great Crosby, is a section of Keuper marls, the only one existing for many miles around. The marls are overlain by Low-level Boulder-clay of the usual type, and between it and the marl is a deposit from 3 to 4 feet thick, which at first sight is not readily distinguishable from the marls, but which a careful examination of the excavations from time to time as they progressed, showed to be a distinct bed. In this bed, lying at all angles, were found large blocks of sandstone, some of which were grooved and striated in an unmistakable manner. The matrix in which they were imbedded was of the same constitution as the marl, and evidently formed out of it, showing in places strong evidences of contortion and kneading up. The sandstone blocks belonged to the Keuper formation, and some of them were very similar to bands intercalated in the marls near the bottom of the excavation. No erratic pebbles or boulders of any sort were found in this kneaded-up marl, whereas the Low-level Boulder-clay is full of them.

The Author considered that the only feasible explanation of the phenomenon was that the marl had been worked up into a grey clay by the passage over it of land-ice, which had broken off the sandstone-bands at their outcrops, forcing the blocks into the disturbed or worked-up marl. These outcrops, concealed by a mantle of Low-level Boulder-clay, must be to the northward, and therefore the blocks have travelled in the same direction approximately as the track of the striations on the neighbouring rocks.

In conclusion, he contended that all the evidence points to the fact before insisted upon, that the intensest period of cold preceded the deposition of the Low-level Boulder-Clay, which is clearly a marine deposit.

3. "The North-Wales and Shrewsbury Coal-fields." By D. C. Davies, Esq., F.G.S.

After discussing the origin of Coal-beds, and the causes of their variation in structure and quality, the Author proceeded to describe the North Wales and Shrewsbury Coal-field, which consists of three parts :—(1) The Shrewsbury field south of the Severn, exclusively composed of Upper Coal-measures ; (2) the tracts north of the Severn, extending from near Oswestry to north of Wrexham ; and (3) the Flintshire Coal-field. The first and second are separated from each other by the alluvial plain of the Severn and Vyrnwy, and the second and third by the Great Bala and Yule faults.

Some remarks on the scenery of the Welsh border-land followed, and then a general section of the Carboniferous system, as developed

in the country described, was given, the Permian beds being included, as the Author considered them the upper portion of one great division of Palæozoic time. The section was as follows, with the maximum thickness of each subdivision :—

Thickness in yards.

1.	Dark red Sandstone	210	
2.	Ifton or St. Martin's Coal-measures	75	Permian, 590 yards.
3.	Red marls with calcareous matter	180	
4.	Green rocks and Conglomerates	125	
5.	Upper Coal-measures	80	
6.	Cefn rock to Cefn coal	100	Coal-measures, 665 yards.
7.	Cefn coal to Lower yard-coal	270	
8.	Lower yard-coal to Chwarcle coal	80	
9.	Chwarcle coal to Millstone Grit	135	

1255 yards.

A detailed description of the strata was next given, beginning with the lowest, together with details of each coal-seam as worked in various parts of the field. After describing the beds from the Millstone Grit to the Cefn rock in the North-Wales coal-field, the Author proceeded to notice the Upper Coal-measures and Permian strata in the Shrewsbury area, and showed that no break exists between the two, the former passing gradually into the latter. He then discussed the probability of Lower Coal-measures existing beneath the upper beds near Shrewsbury, and showed from sections that the existence of the lower measures might be anticipated. A similar inquiry as to the presence of the Coal-measures beneath the New Red Sandstone of the Vale of Clwyd should also, in the Author's opinion, be answered in the affirmative.

The organic remains found in the different beds were briefly noticed, and then the faults of the district were discussed at some length. The principal faults run north and south, with an upthrow to the east, but are crossed by lines of fracture running east and west.

In conclusion, the correlation of the strata in the North Wales and Shrewsbury coal-fields, and especially of the coal-seams, with the beds found in other parts of Great Britain, was discussed, and a section was given to show the representation of the different measures in various coal-basins. The Author was disposed to adopt four subdivisions rather than three only, as usually accepted, and pointed out some of the characteristics of each subdivision.

XII. *Intelligence and Miscellaneous Articles.*

ON THE DEPTH TO WHICH DAYLIGHT PENTRATES IN SEA-WATER. BY MM. H. FOL AND ED. SARASIN.

IN a previous paper * we gave an account of some experiments which we had made in the Lake of Geneva, with a view to determine the limit of penetration of sunlight in water, and we announced our intention of making similar experiments in the sea.

* Phil. Mag. January 1885, p. 70.

Thanks to the kind assistance of Dr. J. Barrois, director of the zoological station of Villefranche-sur-mer, the 'Albatros,' despatch boat of the French Navy, was placed at our disposal for several days. The intelligent and ready cooperation of the lieutenant of the 'Aboiville,' the commander of this vessel, and of all the officers, greatly contributed to the success of these delicate experiments.

Our mode of proceeding was the same as in the experiments on the Lake. A Monckhoven gelatinobromide-of-silver plate was immersed to a given depth, in the apparatus, which remained open during a fixed time. On this occasion we were obliged to preserve the sensitive layer from the chemical action of the sea-water by covering it with a thick coating of varnish. The light acted from the back of the plate and through the thickness of the glass. Repeated washings with spirits of turpentine and absolute alcohol sufficed to remove the varnish before proceeding to develop. As on the former occasion, we employed oxalate of iron as the developing agent, which in every case was allowed to act for ten minutes.

The experiments were made on the 25th and 26th of last March, and were favoured by bright and calm weather. We found the depths we wanted, that is to say from 400 to 600 metres, off Cape Ferrat, which protects the entrance to the Bay of Villefranche. Leaving unnoticed the plates of minor interest, we will quote the following, which appeared to us sufficient to solve the question.

a. Between 10h 30m and 10h 40m a plate exposed at a depth of 200 metres to begin with ; the boat drifting away from the shore we were obliged to let out 60 metres more rope in order to prevent the premature closing of the apparatus.
b. From 12.45 to 12 50 at a depth of 280 m.
c. Between 11.30 and 11.40 at a depth of from 345 to 350 m.
d. Between 10.55 and 11.5 at a depth of 360 m.
e. From 10.15 to 10.25 at a depth of 380 m.
This experiment was made under especially favourable circumstances ; there was neither wind nor swell, the boat remained absolutely motionless, the line perfectly vertical, so that we were not obliged to let out the line throughout the time of exposure.
f. From 1.20 to 1.30, under a cloudy sky, but still luminous enough, at a depth of 405 to 420 m.
All these plates, with the exception of plate *f*, were exposed while the sun was shining brightly.

On developing, the plates *a* and *b* proved to be greatly over-exposed. On the plates *c*, *d*, and *e*, the strength of the impression went on diminishing in a ratio corresponding very regularly with the increase of depth. On the plate *e* the strength of the impression was notably inferior to that produced by an exposure during the same length of time to the air on a clear night with no moon. It is comparable to that produced by an exposure of half the time, say of five minutes only, under these latter conditions.

Lastly, the plate *f* did not bear the least trace of any impression whatever. It is no doubt to be regretted that this last experiment did not take place, like the others, under a perfectly clear sky. But the impression on plate *e*, at 380 m., was already so faint that

we may conclude from it, with sufficient certainty, that the extreme limit could not have been more than 20 metres lower. Moreover, the experiments made in the Lake of Geneva have shown that the dispersion of sunlight by a light layer of clouds does not cause any considerable diminution in the depth to which it can penetrate in water.

We believe we are justified in concluding from our experiments that, in the month of March, in the middle of the day and in bright sunlight, the last glimmers of daylight are extinguished at 400 metres from the surface, in the Mediterranean.

After these results, those of the experiments which we have still continued in the Lake of Geneva, since the publication of our previous notice, have scarcely more than a local interest.   To the absorption peculiar to the water is in this case added that resulting from particles in suspension, more or less abundant according to the level.   We hope, however, to determine an interesting point relative to the influence exercised by the seasons on the degree of transparency of these waters.

We know that the experiments of M. Forel have shown that albumenized silver paper is blackened, in winter, at a depth of 100 metres, whilst in summer it undergoes no alteration at a depth of 45 metres.   It would be interesting to ascertain whether this variation of transparency with the season is peculiar to the superficial layers, or if the same law also holds good at lower levels.

On the 18th of March of this year we repaired to the middle of the Lake in the 'Sachem,' a steam-yacht belonging to M. E. Reverdin, which her owner had kindly placed at our disposal. As in the former experiments on the lake, M. F. A. Forel kindly volunteered to accompany and assist us. The weather was fairly bright; a light layer of clouds dispersed the light without completely stopping the direct rays of the sun. The exposure of the following plates was made in the manner described in our former paper :—

Plate 10 : from 9h 20m to 9.30, at a depth of 158 metres.
Plate 11 : from 10.0 to 10.10, at a depth of 192 metres.
Plate 12 : from 10.30 to 10.40, at a depth of 235 metres.
Plate 13 : from 11.10 to 11.20, at from 240 to 245 metres.
Plate 14 : from 11.48 to 12.23, at from 280 to 300 metres.

The time of exposure was therefore uniformly ten minutes in each case excepting the last, which remained uncovered, at 280 m., during thirty-five minutes.   Nevertheless not the slightest trace of an impression is visible, either upon this plate or upon plates 13 and 12.   Plate 11 shows a very faint impression, somewhat like that of plate *e* at 380 m. in the sea.   Lastly, plate 10 at 158 m. is acted on to about the same extent as plate *e*. We place the extreme limit of penetration of daylight in the Lake of Geneva in winter at about 200 metres.

It follows from a comparison between this series of experiments and the preceding, that light does not penetrate in March more than 20 or 30 m. lower than in September ; in the month of August the difference is perhaps a little greater.   Accordingly the strata of

water below 100 metres do not obey the law of variation of transparency established by M. Forel for the more superficial layers.

Compared with the series of plates exposed in the Lake, the series which we have brought back from the Mediterranean show a more slow and regular gradation, which leads us to think that, whilst in the Lake the light would be quickly intercepted by the more or less turbid deep layers, in the Mediterranean the absorption due to the pure water alone would be the principal, if not the only factor in the arrest of the luminous rays.—*Comptes Rendus*, April 13, 1885.

ON THE ELECTRICAL CONDUCTIVITY OF SOLID MERCURY AND OF PURE METALS AT LOW TEMPERATURES. BY MM. CAILLETET AND BOUTY.

The electrical resistance of pure metals increases with the temperature. From the experiments of Matthiessen * and those of M. Benoit †, the mean coefficient of increase in the resistance for one degree between 0° and 100° differs little in various metals, and is only slightly removed from $\frac{1}{273}$, that is, the coefficient of the expansion of gases. If the same law held at low temperatures, the resistance of a metal, varying like the pressure of a perfect gas under constant pressure, would furnish a measure of the absolute temperature, and would cease to exist at absolute zero.

Our experiments have been made with mercury and various other pure metals. The mercury was contained in a spiral capillary glass tube terminating in two large reservoirs in which dipped two thick electrodes of amalgamated copper. The reservoir of a hydrogen-thermometer‡ was in the interior of the spiral; and the whole being immersed in ice, or in a bath of methylic chloride or of ethylene cooled by a current of air, according to the method which one of us has given. To work with another metal, copper for instance, the wire is coiled in a spiral form on an ebonite tube in which are long slits, so as to be certain that the liquid was properly mixed, and that the bath and the resistance were measuring at the same temperature.

We have only made relative measurements. The resistance investigated was compared with that of a column of mercury at 0°, by means of a Wheatstone's bridge and a very sensitive reflectinggalvanometer. The following are the results which we have obtained :—

1. *Mercury.*—The empirical formula given by MM. Mascart, De Nerville, and Benoit, for the apparent resistance of mercury in glass above 0°, also holds for the freezing-point. When it solidifies, its conductivity suddenly increases in a ratio, which at −40° is equal to 4·08. The resistance of solid mercury decreases,

* Proceedings of the Royal Society, vol. xi. p. 516.
† *Comptes Rendus*, vol. lxxvi. p. 342 (1873).
‡ Hydrogen-thermometer of constant volume, in which the pressure at 0° was 509·3 millim.

then, regularly as the temperature sinks; between $-80°$ and $-92°{\cdot}13$ it is represented by the formula

$$r_t = r_{-40}\,\frac{1+at}{1-40a},$$

in which t is the temperature on the centigrade-scale with

$$a = 0{\cdot}00407.$$

This coefficient of variation a, which is almost five times that for liquid mercury, is very near that of other pure liquids in the solid state.

2. *Silver, Aluminium, Magnesium, Tin.*—For these various metals the resistance is represented by the formula

$$r_t = r_0(1+at);$$

and the values of a, deduced from numerous experiments made at various temperatures, are the following :—

Metal.	a.	Range of temperature.
Silver	0·00385	$+29{\overset{\circ}{\cdot}}97$ to $-10\overset{\circ}{1}{\cdot}75$
Aluminium	0·00388	$+27{\cdot}77$ to $-\ 90{\cdot}57$
Magnesium....	0·00390	0 to $-\ 88{\cdot}31$
Tin	0·00424	0 to $-\ 85{\cdot}08$

These values of a, which are very near those for the same bodies near $0°$, according to Matthiessen's experiments, are almost identical for the first three metals; the value of a for solid mercury is between the value common to magnesium, aluminium, and silver, and that for tin.

3. *Copper.*—The most complete experiments are those which we have made with copper. They gave the following values for a deduced from a series of thirty measurements, which have been divided into three groups :—

	a.	Range of temperature.
Copper .... $\Big\{$	0·00418	$\overset{\circ}{0}$ to $-\ 58{\cdot}22$
	0·00426	$-\ 68{\cdot}65$ to $-101{\cdot}30$
	0·00424	$-113{\cdot}08$ to $-122{\cdot}82$

These values are a little greater than those which follow from the formulas of Matthiessen and of M. Benoit for temperatures near $0°$*. The variation of resistance is almost absolutely regular, and would enable us, in case of need, to dispense with a hydrogen-thermometer in measuring temperatures between $-20°$ and $-123°$. No appreciable variation of a is observed at this latter temperature, which would seem to indicate that the agreement, at any rate approximate, of the hydrogen-thermometer and the copper spiral thermometer might be pursued still further.

4. *Iron, Platinum.*—Both these metals differ greatly from the others in the variation of their resistance above zero; they diverge from it in the same direction at low temperatures. The formula

$$r_t = r_0(1+at)$$

---

* $a = 0{\cdot}00367$ (Matthiessen); $0{\cdot}003637$ (Benoit).

holds for iron from 0° to −92°, with $a = 0.0049$, but it does not hold for platinum. The value of α deduced from the formula (2), which near 0° would be about 0·0030, increases as the temperature sinks, and becomes 0·00342 for a lower limit equal to −94°·57; hence platinum approaches the other pure metals as the temperature sinks.

In conclusion, our experiments prove that the electrical resistance of most metals decreases regularly when the temperature sinks from 0° to −123°, and that the coefficient of variation is appreciably the same for all. It seems probable that this resistance would become extremely small, and therefore the conductivity very great, at temperatures below −200°, although our experiments do not enable us to form any precise idea of what would take place in those conditions.—*Comptes Rendus*, May 11, 1885.

OPTICAL METHOD FOR THE ABSOLUTE MEASUREMENT OF SMALL LENGTHS. BY M. MACÉ DE LÉPINAY.

M. Mouton[*] gave an ingenious method for measuring, in wavelengths, the thickness of a quartz plate cut parallel to the axis, which depends on a determination, by means of a known grating, of the wave-lengths of Fizeau and Foucault's dark bands. Unfortunately it depends on our really very imperfect knowledge of the values $n'-n$ of the two indices of quartz for different radiations, and cannot therefore give numbers which are exact to within $\frac{1}{1000}$. On the other hand, the corrections for temperature are considerable : $\frac{1}{10000}$ for a degree Centigrade.

I. The method which I have used, which is analogous in principle to the preceding, depends on an observation of Talbot's bands[†], obtained by intercepting half the pencil of sunlight which falls on a known grating by a quartz plate with true parallel faces. The spectra *deflected on the side of the plate* are then channelled with lines, in general extremely fine, but which for that very reason tend to a point as exact as that of the spectrum. By using the third spectrum of a grating of $\frac{1}{500}$ millim., I have been able to apply the method directly to a quartz plate parallel to the axis, about 4 millim. in thickness. It is known that the wave-lengths corresponding to the centre of each of these dark bands are related to the thickness of the plate e, and the index n, by the formula

$$2\frac{n-1}{\lambda}e=p,$$

p being an even whole number, which measures the number of the order of the fringe observed, and which increases by two units in passing from one band to the other, counting from red to violet. We thus obtain as many values very near the desired thickness as are observed, and the mean is taken.

In the preceding formula the index is directly given to within

[*] *Journal de Physique*, vol. viii. p. 393 (1879).
[†] *Journal de Physique*, vol. i. p. 177 (1872).

one or two units near the fifth decimal place, by either of the formulæ[*]

$$(n - 1{\cdot}52642)(\lambda - 1{\cdot}5182 \times 10^{-5}) = 7{\cdot}7733 \times 10^{-7},$$

$$(n' - 1{\cdot}53519)(\lambda - 1{\cdot}5504 \times 10^{-5}) = 7{\cdot}8594 \times 10^{-7};$$

calculated by taking the mean of the very concordant measurements of the indices made by Rudberg, Mascart, and Van der Willigen, taking for the wave-lengths the means of the measurements made by Mascart, Ditscheiner, Van der Willigen, and Ångström; the latter numbers were transformed so as to correspond to the wave-length $\lambda_{D_2} = 5{\cdot}888 \times 10^{-5}$ adopted by M. Mascart. The constant of the grating having been determined each time so as to satisfy this condition, we see that the thicknesses are provisionally measured as a function of what M. Mouton calls *Fraunhofer's millimetre*.

II. A double correction for temperature must be introduced in the thicknesses thus calculated. If by θ we denote the temperature to which correspond the indices given by the formulæ above, by t that at which the measurements were made, the thickness e_0, at 0° of the plate, should be calculated by the formula

$$2e_0(1 + kt)(n + v'\theta - vt - 1) = p\lambda;$$

k, v, and v' being coefficients determined, the first by M. Benoit, the two others by M. Dufet[†]. It is more simple and just as exact to correct the thickness e_0, originally calculated by one or other of the two simplified formulæ,

$$e_0 = 0{\cdot}999741(1 - 0{\cdot}0000019\,t)e \text{ ordinary rays,}$$

or $\qquad e_0 = 0{\cdot}999709(1 - 0{\cdot}0000001\,t)e$ extraordinary rays.

These two formulæ[‡] apply to the case in which the plate is cut parallel to the axis.

III. I applied this method to two quartz plates cut parallel to the axis made by Hoffmann. The thinnest of them measured directly (123 bands observed, ordinary rays) gave

$$e_0 = 0{\cdot}402958 \text{ cm.} \pm 0{\cdot}000001.$$

On the other hand, we measured the difference in thickness of two plates (123 bands observed, extraordinary rays). From this was deduced for the thickest plate,

$$e_0 = 0{\cdot}602316 \text{ cm.} \pm 0{\cdot}000003.$$

IV. We may add that this method may lead to a new determination of the absolute value of the wave-length of the ray D_2. The thickness of the second plate, which M. Benoit kindly measured with the apparatus of the Bureau international des Poids et Mesures, was found equal to 0·60236 to within 1^μ or 2^μ. From this we get for the wave-length of the line D_2, the number

$$\lambda = 5{\cdot}8884 \times 10^{-5},$$

which is exact to within $\frac{1}{3000}$, and is very near that of Ångström (5·8889).—*Comptes Rendus,* June 2, 1885.

[*] Cornu, *Annales de l'Ecole Normale supérieure,* vol. ix. p. 42 (1880).

[†] *Journal de Physique,* 2nd series, vol. cxi. p. 252 (1884).

[‡] It has been assumed that $\theta = 20°$. As this temperature is scarcely known to within 4° or 5°, there is an uncertainty of about $\frac{1}{25000}$.

XIII. *The Polymerization of the Metallic Oxides. By* Louis Henry, *Professor of Chemistry in the Catholic University of Louvain*[*].

Introduction.

ONE of the principal objects of Physical Science, in fact its principal object, is to determine the natural relation of things. It is by comparisons logically established between the things themselves that these relationships are disclosed. An essential condition to be observed in researches of this kind is to compare only those objects which are really comparable. Stated in the terms of chemical science, this general condition of all work undertaken with a truly scientific object consists in establishing a comparison only between the chemical molecules themselves. Molecules are, in fact, for the chemist the veritable chemical individuals—they are the bodies themselves in their simplest, and at the same time their most complete, expression. Molecules find a graphic representation simple and concise, and sometimes even sufficiently perfect, and in every case susceptible of a great degree of precision, in the chemical formulæ at present in use.

Formulæ, however, only maintain their full and complete utility so long as they are the exact and complete representation of the molecules of bodies,—of bodies between which chemical actions occur, of bodies which we possess in reality, and which are the veritable objects of our comparisons. This representation becomes exact and complete only when the for-

mula indicates the three facts fundamental to the being of the molecule, viz. (1) the nature of its constituent elements, (2) the actual number of atoms of each present, and (3) their combining proportion.

We are still far from this degree of completeness. Our knowledge of bodies from the molecular point of view is very incomplete, and especially so as regards Mineral Chemistry. Not only is the number of compounds, of which the constitution and structure have been successfully determined, very limited, but there are a great number, I might even say the greater number, to which we are still unable to attribute a formula expressing in a satisfactory manner the true size and real weight of the molecule. The formulæ used in Mineral Chemistry are in the majority of cases only the empirical formulæ, indicating merely the nature and relative weights of the atoms of the elements in the compound, and are wholly silent as to the absolute quantity of matter, or the actual number of atoms present in the molecule. They do not give therefore any idea either of its size, or of its absolute weight, or of its internal structure. The properties of compounds do not depend on chance ; they depend chiefly no doubt on the nature of the elements constituting the molecule, but they are also conditioned by the internal structure of the latter, and by its size and weight.

It is to Berzelius that we owe the idea of *isomerism,* without which a rational study of the innumerable compounds of carbon would be absolutely unattainable. However it may be, each of these three great factors in the diversity of compound bodies exercises a special and preponderating influence on certain classes of properties. If, on the one hand, the chemical activity of a given compound depends especially on the essential nature of the atoms constituting the molecule, and on the constitution of the latter, on the other, an increase in its weight powerfully affects the physical and mechanical properties.

Whatever may be the specialization of this dependence, the properties of a body, considered individually or relatively, the one in relation to the other, their analogies and their differences, can only be well understood when we know the size of the molecule.

Just as the adoption of rational and true formulæ for the various compounds may render great service in a systematic study, so in the same degree will the adoption of imperfect formulæ, artificial and false, or even incomplete and expressing only simple relations, lead to results which are untrue. Such formulæ mislead by obscuring, or even by totally concealing,

the real relations of bodies. They create imaginary relationships, removing apart those bodies which ought to be brought together, and bringing those together which ought to be kept apart. Our formulæ should be like glasses of a perfect transparency, through which the bodies should be seen as they are, and not like screens to hide, or disguises to disfigure.

Most formulæ now in use refer to the perfect gaseous state. These formulæ are undoubtedly excellent for bodies of which the normal state is gaseous ; but their exclusive use is insufficient, and creates a void to be regretted in the comparative study of bodies, both from the individual and general point of view. The number of bodies naturally gaseous is in fact very limited ; and if the number of those capable of becoming so is very considerable, still there are many which are not, and with an absolute or relative fixity resist the highest temperatures, or are decomposed.

Our usual molecular formulæ are therefore necessarily insufficient, being inapplicable to numerous compounds, and to the various states which the same body is capable of assuming. These formulæ, referring to the perfect gaseous state, do not tell us anything of the molecular nature of these same bodies when in the ordinary condition. Thus it is, to appeal to classical examples, with the formulæ of sulphur, and of the fatty acids, or at least with the first terms of the latter series.

It is in all respects desirable that the molecular formulæ of bodies should refer to their natural state, and that the several formulæ should be determined for the various physical states which the bodies can either naturally or artificially assume. That is the only way to avoid misconceptions, artificial difficulties, false analogies between unlike bodies, and to retain for various compounds their own physiognomy.

There is no teacher of Chemistry who has not frequently noticed, both in mineral and in organic chemistry, differences in the properties of bodies, which are often most profound, and totally beyond theoretical prevision, notwithstanding that the bodies are apparently related as regards their formulæ and the analogy of their composition. It is easy to say that there are exceptions and anomalies. But in spite of these words, the difficulties still exist in all their entirety, embarrassing the mind of both teacher and taught. The greatest caution should be used in qualifying exceptional and anomalous facts; otherwise confusion is created in the mind, and place is given to chance in the occurrence of natural facts : it is the ruin of law and general principles. It is well to remember the old adage, applicable in the physical as well as

in the natural world, that exceptions prove the rule. True exceptions, true anomalies, have no real existence ; these apparent deviations in the effects of a general known cause are due to the influence of other causes, acting simultaneously, the existence of which remains momentarily hidden from view.

Among the difficulties which are met with in the comparative study of bodies, there are some which are peculiarly embarrassing, and which it would be chimerical to try to solve under present circumstances. But there are others, and I believe a very considerable number, which are purely artificial, without real foundation ; difficulties which would vanish of themselves if we only had a less imperfect knowledge of the bodies with which they occur—if, in fact, the chemical signification of these bodies molecularly in relation to others were only clearly and surely defined.

This point of view, from which bodies should be studied, is not absolutely new. Sulphur and the fatty acids, especially acetic acid, are well-known examples of substances which have been clearly distinguished in their various physical states. Moreover, the determination of the relative molecules of bodies in their various states also touches on a question of still greater interest, viz. that of the chemical relationships of the various physical states in which they occur.

The molecular formulæ at present in use refer to the gaseous state, and the principal method of determining them depends on the vapour-density. This process, simple and expeditious, is undoubtedly excellent in all cases in which it is applicable. Others, however, are necessary for the determination of molecules in a state other than that of a perfect gas. It is in the complete study of bodies in their various conditions that we should find indications sufficient for information as to their molecular nature. The several circumstances which characterize the chemical molecule, both chemically and physically, are in intimate connection, and to determine this molecule we can appeal to all connected therewith, either in its past, present, or future : in its *past*, to examine its mode of formation and the various circumstances bearing on its chemical origin ; in its *present*, to carefully investigate the whole of its properties—physical, mechanical, and chemical ; in its *future*, to study the reactions in which it may take part, the products of its decomposition, its metamorphoses, &c.

This complete study of bodies, from both the statical and dynamical point of view, always gives, though it may be imperfect, valuable information for solving our present problem. It is, however, necessary to say, that when I speak of actual molecules and of actual molecular formulæ, I do not

forget that these molecules, as well as the formulæ which express them, are really only relative. We do not know, and we shall never know, that which is truly and absolutely a molecule, for we cannot and never shall be able to obtain one singly and alone. We possess, and we shall always possess, only groups of molecules. The character of reality which we wish to give to our molecules and to our formulæ is essentially, then, a relative one. What we have to determine are real relationships between real bodies. These relationships of analogy and difference remain practically the same if, in the impossibility of verifying them between the bodies themselves, we seek for them between the same bodies in a modified condition ; modified simultaneously, however, and in a similar manner. It results from these considerations that it is of great importance to examine chemical phenomena from the molecular point of view. To establish real molecular formulæ for bodies (*i. e.* formulæ truly and universally *comparable*) is therefore an object eminently worthy of attention. It is this idea which has induced me to undertake a lengthened series of theoretical and experimental studies on compounds in both mineral and organic chemistry, and more particularly as regards the metallic oxides.

The Peculiar Character of the Metallic Oxides.

A comparative examination of the oxides and chlorides leads to a general fact. Chlorides are fusible compounds, and, with few exceptions, volatile. It has been long observed that chlorine gives wings to the metals, as one may say. Volatility is especially noticeable in the chlorides of the fixed elements, and particularly of the metals. The corresponding oxides, on the contrary, are distinguished by their fixity and infusibility, either absolutely or relatively. The following table shows that this difference is general:—

	Molecular weight.	Physical state.	Fusibility.	Volatility.
BCl_3	117	Liquid.	....	Boils 17°.
B_2O_3	70	Solid.	Fuses 577°.	Fixed.
$SiCl_4$	170	Liquid.	....	Boils 59°.
SiO_2	60	Solid.	Fusible in oxyhydrogen flame.	Fixed.
$TiCl_4$	192	Liquid.	....	Boils 135°.
TiO_2	82	Solid.	Infusible.	Fixed.
$ZrCl_4$	231·5	Solid.	Fusible.	Sublimable.
ZrO_2	121·5	Solid.	Infusible.	Fixed.
$SnCl_4$	260	Liquid.	....	Boils 115°·4.
SnO_2	150	Solid.	Infusible.	Fixed.
$SnCl_2$	189	Solid.	249·3.	617°–628°.
SnO	134	Solid.	Infusible.	Fixed.

Table (*continued*).

	Molecular weight.	Physical state.	Fusibility.	Volatility.
NbCl$_5$	271·5	Solid.	Fuses 194°.	Boils 240°·5.
Nb$_2$O$_5$	174	Solid.	Infusible.	Fixed.
TaCl$_5$	359·5	Solid.	Fuses 211°·3.	Boils 241°·6.
Ta$_2$O$_5$	444	Solid.	Infusible.	Fixed.
Al$_2$Cl$_6$	268	Solid.	Very fusible.	180°.
Al$_2$O$_3$	103	Solid.	{ Fusible in oxyhydrogen flame. }	Fixed.
Al$_2$Br$_6$	535	Solid.	Fuses 93°.	Boils 260°.
Al$_2$I$_6$	817	Solid.	Fuses 125°.	Boils 350°.
Fe$_2$Cl$_6$	325	Solid.	Fuses 306°–307°.	Easily volatile.
Fe$_2$O$_3$	160	Solid.	Infusible.	Fixed.
FeCl$_2$	127	Solid.	....	Volatile.
FeO	72	Solid.	Infusible.	Fixed.
Cr$_2$Cl$_6$	317·8	Solid.	....	Volatile.
Cr$_2$O$_3$	152·8	Solid.	Infusible.	Fixed.
CrO$_2$Cl$_2$ ...	155·4	Liquid.	....	Boils 118°.
CrO$_3$	100·4	Solid.	Fuses about 300°.	Decomposes.
WCl$_5$	359·5	Solid.	Fuses 248°.	Boils 275°·6.
WCl$_6$	395	Solid.	Fuses 275°.	Boils 346°·7.
WCl$_4$O ...	342	Solid.	Fuses 210°·4.	Boils 127°·5.
WO$_3$	232	Solid.	Fuses at forge-heat.	Fixed.
VCl$_4$	193·3	Liquid.	{ Does not solidify at −18°. }	Boils 154°.
VO$_2$	83·3	Solid.	....	....
VOCl$_3$	173·8	Liquid.	{ Does not solidify at −15°. }	Boils 126°·7.
SeCl$_4$	221·5	Solid.	{ Easily volatile, without fusion. }	....
SeOCl$_2$	166·5	Liquid.	....	Boils 179°·5.
SeO$_2$	111	Solid.	Infusible.	{ Volatile at 300° without melting.
TeCl$_4$	270	Solid.	Fuses 224°.	Boils 414°.
TeO$_2$	160	Solid.	Fusible.	{ Less volatile than tellurium.
AsCl$_3$	181·5	Liquid.	{ Does not solidify at −29°. }	Boils 134°.
As$_2$O$_3$	198	Solid.	Volatile without fusion.	Boils 200°.
SbCl$_3$	228·5	Solid.	Fuses 73°·2.	Boils 225°.
Sb$_2$O$_3$	282	Solid.	Fuses red-heat.	Volatile below 1560°.
SbCl$_5$	299	Liquid.	Solid at 0°.	{ Volatile into SbCl$_3$ +Cl$_2$.
Sb$_2$O$_5$	324	Solid.	Nonfusible.	Nonvolatile.
BiCl$_3$	316·5	Solid.	Fuses 227°.	Boils 427°–439°.
Bi$_2$O$_3$	468	Solid.	Fusible.	Fixed.
HgCl$_2$	271	Solid.	Fuses 265°.	Boils 295°.
HgO	216	Solid.	Infusible.	Decomposes.
Hg$_2$Cl$_2$	471	Solid.	{ Sublimes 400°–500° without melting. }	....
Hg$_2$O	416	Solid.	Infusible.	Decomposes.
Cu$_2$Cl$_2$	198	Solid.	Fuses 434°.	Boils 954°–1032°.
Cu$_2$O	143	Solid.	Fuses at red-heat.	Fixed.
CuCl$_2$	134·5	Solid.	Fuses 498°.	Decomposes.
CuO	79·5	Solid.	{ Fuses at bright red-heat, with decomposition. }	....

Table (*continued*).

	Molecular weight.	Physical state.	Fusibility.	Volatility.
$PbCl_2$	278	Solid.	Fuses 498°.	Boils 861°–954°.
PbO.........	223	Solid.	Fuses about a red-heat.	Volatile at white-heat.
Ag_2Cl_2......	287	Solid.	Fuses 451°.	....
Ag_2O	232	Solid.	Infusible.	Decomposes.
$CaCl_2$	111	Solid.	Fuses 719°.	....
CaO.........	56	Solid.	Infusible.	Fixed.
$SrCl_2$	158·5	Solid.	Fuses 825°.	....
SrO	103·5	Solid.	Infusible.	Fixed.
$BaCl_2$	208	Solid.	Fuses above 860°.	....
BaO.........	153	Solid.	Fusible in oxyhydrogen flame.	Fixed.
$MgCl_2$	95	Solid.	708°.	Volatile.
MgO	40	Solid.	Infusible.	Fixed.
$ZnCl_2$	136	Solid.	Fuses 262°.	Boils 676°–683°.
ZnO.........	81	Solid.	Infusible.	Fixed.
$CdCl_2$	183	Solid.	Fuses 541°.	Boils 861°–954°.
CdO.........	128	Solid.	Infusible.	Fixed.
UCl_2	191	Solid.	....	Volatile.
UO	136	Solid.	Infusible.	Fixed.
$NiCl_2$	129·75	Solid.	Sublimes without fusion.	....
NiO	74·75	Solid.	Infusible.	Fixed.
$BeCl_2$	80·25	Solid.	Fuses 585°–617°.	Volatile below 520°.
BeO.........	25·25	Solid.	Infusible.	Fixed.
$ThCl_4$	376	Solid.	....	Sublimes.
ThO_2	266	Solid.	Infusible.	Fixed.

As already stated, this difference in properties is observed especially in the oxides and chlorides of positive elements, and in general in elements having a metallic brightness. It may be noted by the way that it appears to be the greater the higher the atomicity of the metal.

Whatever may be its meaning, this physical difference is, by its generality, one of the most remarkable facts in statical chemistry, strange and, at first sight, quite exceptional.

The properties of compound bodies do not appear by chance; they are only the final result of the properties of the constituent elements—a result more or less modified in consequence of the physical phenomena of combination. Chemical compounds are therefore really mixtures of a special kind. It cannot be denied that the properties of compounds are closely related to those of their principal constituents. The differences between certain elements occur again with greater or less fidelity in their corresponding and comparable compounds. That being so, the behaviour of the metallic oxides is especially

surprising when compared with the chlorides of the same elements.

The difference between the volatility of oxygen and chlorine is enormous. The former, until recently, was considered as a permanent gas; the other, on the contrary, is easily condensed, and only becomes gaseous at $-33°·6$ (Regnault). An atom of oxygen weighs 16, and that of chlorine 35·5. The molecular weights of the chlorides are consequently much greater than those of the corresponding oxides. Now, of mechanical or physical properties, there is not one which is more directly dependent on the molecular weight than fusibility and volatility.

Bearing these facts in mind, we are justified in formulating *à priori* the following propositions :—(1) Oxygen and chlorine are both of them elements which are endowed with great volatility as compared with other elements. The oxides and the chlorides ought, therefore, to be volatile compounds. (2) Volatility exists to a greater degree in oxygen than in chlorine. The oxides ought, therefore, to be more volatile than the corresponding chlorides. The oxides ought frequently to be very volatile, or even gaseous, at the ordinary temperature.

These theoretical deductions are, in fact, realized in a good number of oxygenated and chlorinated compounds, particularly in the case of elements or radicals which are negative or metalloidal, *e. g.* As, Os, Ru, &c.

	Molecular weight.	Physical state.	Volatility.
OO	32	Perfect gas ; formerly considered permanent.	
OCl_2.........	87	Gas, easily condensed.	
SO_2	64	Gas.	Boils $-10°$.
$SOCl_2$	119	Liquid.	Boils $82°$.
SO_3	80	Solid.	Boils $46°$.
SO_2Cl_2.....	135	Liquid.	Boils $82°$.
CO_2	44	Gas.	Boils $-78°$.
$COCl_2$	99	Liquid.	Boils $+8°$.
CCl_4.........	154	Liquid.	Boils $+76°$.
C_2Cl_6	237	Solid.	Boils $182°$.
C_2Cl_4O * ...	182	Liquid.	Boils $118°$.
OsO_4	263	Solid.	Volatilizes about $100°$.
RuO_4	168	Solid.	Volatilizes $100°$.
As_2O_3	198	Solid.	Volatilizes $200°$.
PCl_5.........	208·5	Solid.	Boils $148°$ †.
PCl_3O......	153·5	Liquid.	Boils $110°$.
WCl_6	395	Solid.	Boils $346°$.
WCl_4O ...	342	Solid.	Boils $227°$.

* $CCl_3 . COCl.$ † Decomposing into $PCl_3 + Cl_2.$

Relationships of a similar kind, as regards volatility, are observed between the oxides and the chlorides of the bivalent radicals C_nH_{2n}, which are the most analogous to the metals, for example:—

		Molecular weight.	Volatility.
C_2H_4O	Aldehyde	44	Boils 21°
	Ethylene oxide	,,	,, 13·5
$C_2H_4Cl_2$ ...	Ethylidene chloride....	99	,, 60
	Ethylene chloride	,,	,, 84
C_3H_6O......	Propylene oxide.........	58	,, 35
	Aldehyde	,,	,, 47
	Acetone	,,	,, 56
$C_3H_6Cl_2$ ...	Propylene chloride.....	113	,, 96
	Propylidene chloride...	,,	,, 85
	Acetone chloride	,,	,, 70

Let us now attempt, by the aid of this general idea, to determine, *à priori*, what ought to be the properties of certain particularly interesting oxides.

To CO_2, which is gaseous at the ordinary temperature and boils at $-78°$, corresponds CCl_4, which is a liquid boiling at $+76°$. The difference in volatility between the two bodies is 154°. $SiCl_4$, $TiCl_4$, and $SnCl_4$ boil respectively at 58°, 136°, and 115°. It might therefore be reasonably supposed that the corresponding oxides should be eminently volatile. SiO_2 ought certainly to be gaseous at the ordinary temperature, or at least as gaseous as SO_2, to which it is analogous, and the molecular weight of which is but little different.

	Molecular weight.	Boiling-point.
CO_2	44	$-78°$
SO_2	64	-10
SiO_2	60	nonvolatile.

BCl_3, with molecular weight 117·5, is a liquid boiling at 18°; B_2O_3, with molecular weight 70, ought therefore to be a gas at the ordinary temperature.

Al_2Cl_6 is a solid, which volatilizes about 100°, and ought therefore to have a corresponding oxide Al_2O_3, if not gaseous, at least very volatile, and the same should hold good as regards Fe_2O_3.

$HgCl_2$ (boiling-point 295°) should have a corresponding oxide, HgO (containing a so-called permanent gas in combination with a volatile metal), which, if not gaseous, should at least be much more volatile than $HgCl_2$, or metallic mercury.

The chromates are analogous to the sulphates both in their general composition and crystallographical properties. One would expect, therefore, that the difference between CrO_2O and CrO_2Cl_2 would be similar to that between SO_2O and SO_2Cl_2. Now SO_3 boils at $46°$ and SO_2Cl_2 at $77°$, whilst CrO_2Cl_2 is a liquid boiling at $118°$; and from analogy we should expect CrO_3 to be also a liquid still more volatile, and boiling even below $100°$, whereas CrO_3 is a solid, fusible only at about $300°$. The oxides, in fact, instead of being gaseous at the ordinary temperature, or at least very volatile liquids, as analogy would have led us to expect, are generally solid, and frequently almost infusible. What is the explanation of this fact, so strange in its nature and so important from its generality? I regard no fact, however strange, as abnormal or exceptional. In my opinion anomalies and exceptions have no real existence. They depend most probably, as already stated, on our ignorance of the consequences, under certain conditions, of a general known cause.

The Oxides are not Molecularly Comparable to the Chlorides.

Polymerization of the Oxides.—The chlorides and oxides are almost universally indicated by formulæ which represent these bodies as molecularly comparable. But are the oxides really comparable with the chlorides of the same elements? Is there a real analogy between them, or is this analogy merely artificial, and dependent solely on the notation employed? These are questions which require examination. The chlorides being compounds which are frequently volatile without decomposition, the formulæ assigned to them have usually been deduced from the determination of their vapour-density; so that these formulæ really represent, both in weight and size, the molecules of these bodies, at least in the gaseous state. This is not the case, however, with the metallic oxides. Being fixed, or volatile only at the very highest temperatures, or else decomposing under the action of heat, their vapour-densities are unknown, and cannot be determined. The formulæ universally attributed to the metallic oxides depend solely on analytical determinations. These formulæ are therefore simply empirical, and merely represent the *relations* between the weights of the constituent elements, but are perfectly silent as regards the absolute quantities.

The formulæ of the oxides have thus their origin, and rest on an entirely different basis from the formulæ of the chlorides. There is no authority for attributing to both the same value and signification. The relation between the oxides and chlorides, as represented by the usual formulæ, is purely artificial.

The true oxides RO_x, which are really comparable with the known chlorides RCl_{2x}, are for the most part quite unknown. We only have the polymeric oxides $n(RO_x)$, in which n is a large number. To make this clear, we may take an example from organic chemistry in illustration, viz. the chlorides of ethylene and ethylidene:—

$$\begin{matrix} CH_3 \\ | \\ CHCl_2 \end{matrix} \text{ b.-p. } 60°, \qquad \begin{matrix} CH_2Cl \\ | \\ CH_2Cl \end{matrix} \text{ b.-p. } 84°.$$

Not only are the corresponding oxides, acetaldehyde and ethylene oxide,

$$\begin{matrix} CH_3 \\ | \\ CHO \end{matrix} \text{ b.-p. } 21°, \qquad \begin{matrix} CH_2 \\ \\ CH_2 \end{matrix}\!\!\!>\!\!O, \text{ b.-p. } 13°,$$

known, but also their respective polymers paraldehyde and metaldehyde, as well as the dioxide and polyoxide of ethylene.

{ Paraldehyde . . $(C_2H_4O)_3$, liquid, boiling-point 124°.
{ Metaldehyde . . $(C_2H_4O)_n$, solid, nonvolatile as such.
{ Ethylene dioxide $(C_2H_4O)_2$, solid, boiling-point 102°.;
{ Ethylene polyoxide $(C_2H_4O)_n$, solid, volatile with difficulty.

This interpretation of oxides being admitted, it is no longer a hypothesis, but a fact, that the physical state and thermal properties, notably the fusibility and volatility, are a direct function of the molecular weight, and every abnormal relation, from the physical point of view, between the chlorides and oxides ceases immediately. The infusibility and fixity of the latter, so strange at first sight, return into the natural order of things.

We have, therefore, to prove the following proposition:—

The known oxides, and notably the metallic oxides, are polymers $n(RO_x)$ of the true oxides RO_x, corresponding to the chlorides RCl_{2x}.

Proofs of the Polymerization of the Oxides.

Their Additive Power.—There are no compounds which are more ready to enter into combination than the oxides. In fact, it would not be far from the truth to say that there is no class of compounds with which they are incapable of entering into combination. In mineral chemistry they combine by addition, and often with considerable energy, not only with oxides of a contrary sign—acid oxides with basic oxides,—but with all chemical compounds indiscriminately, whatever may be their special function.

Let us limit ourselves more especially to metallic oxides. They combine not only with the oxides of negative radicals, but also with the most diverse binary compounds—chlorides, bromides, iodides, sulphides, selenides, &c.; with oxysalts in general—hydrates, sulphates, nitrates, carbonates, &c., forming the large series of basic salts of the polyvalent metals. These additive compounds are formed in the most varied proportions; so that the series of basic salts is illimitable. Many of them are marked by a definite composition and by a regular crystalline character; some even occur naturally in the mineral kingdom.

This additive power is observed also, though in a less degree, with the oxides of organic radicals, and notably in the case of the glycollic oxides, $C_nH_{2n}O$, which are so similar in other respects to the metallic oxides RO. The oxide of ethylene combines with its hydrate, glycol $C_2H_4(OH)_2$, with acetic anhydride, with acetyl chloride, with the halogen hydracids, &c. The aldehydes $C_nH_{2n+1}.CHO$ behave in a similar manner.

But let us return to the metallic oxides. Metallic oxides enter into combinations with other metallic oxides which differ in composition, both in the nature of the metal and in the quantity of oxygen. Thus, MgO combines with Al_2O_3 to form spinelle, $MgO.Al_2O_3$. Still more remarkable is the combination of two oxides of the same metal, as in magnetic oxide of iron, $FeO.Fe_2O_3$; red lead, $2PbO.PbO_2$; hausmannite, $MnO.Mn_2O_3$; $SnO.SnO_2$; &c.

Organic chemistry also furnishes examples of this, which are still more curious in so far as we have cases where two oxides, equally oxygenated, combine, as in the case of the double oxide of ethylene and ethylidene discovered by Würtz (*Bull. Soc. Chim.* iv. p. 16), $\left(\begin{matrix}CH_2\\CH_2\end{matrix}\right\rangle O + \begin{matrix}CHO\\CH_3\end{matrix}\right)$. Here we have polymerization properly so called.

In the absence of foreign molecular systems on which they can exercise their additive power, oxides, both organic and inorganic, combine with themselves; and in this combination of a body with itself lies the gist of polymerization in its largest sense. This fact may be illustrated by examples from organic chemistry. Ethylene oxide, $\begin{matrix}CH_2\\CH_2\end{matrix}\right\rangle O$, is a colourless liquid, boiling at 13°.

Two distinct polymers of this compound are known :—(*a*) The so-called diethylene dioxide, $\begin{matrix}CH_2.O.CH_2\\CH_2.O.CH_2\end{matrix}$, is obtained directly from the monoxide and is a crystalline solid, melting-point 9°, boiling-point 102°. (*b*) A polymer, $(C_2H_4O)^n$, obtained by

Würtz (*Compt. Rend.* lxxxiii. p. 1141), is formed sponta-
neously as a white solid crystalline mass, melting-point 56°,
and volatile with difficulty.

In connection with this question there is no body more
interesting than methylene oxide, $CH_2 : O$. The corresponding
chloride, CH_2Cl_2, is a liquid, boiling-point 40°. The oxide itself
should be naturally a gas, but only assumes this state under
the action of heat ; so soon as the heat is withdrawn, it poly-
merizes, and is converted into a white solid mass which is
insoluble in water, and sublimes at 100°, again changing at
higher temperatures into the gaseous CH_2O, as indicated by
its vapour-density. The aldehydes C_nH_x . CHO are especially
characterized by their tendency to polymerization, giving rise
to products differing from the original aldehyde in all their
physical properties—fusibility, volatility, solubility, &c. Acet-
aldehyde may be taken as a type of this class. Under ordinary
circumstances it is a liquid, boiling-point 21°. There are two
distinct polymers known:—

(*a*) *Paraldehyde* is a liquid, boiling-point 124°, and in the
state of gas is represented by $(C_2H_4O)_3$, as proved by its vapour-
density.

(*b*) *Metaldehyde*, $(C_2H_4O)_n$, is a solid, crystallizing in
beautiful needles, which sublime at 100°, and volatilize without
melting at 112–115°, being transformed again into ordinary
aldehyde as indicated by its vapour-density.

Trichloraldehyde, or chloral, CCl_3 . CHO, polymerizes still
more easily. When recently distilled, it is a liquid, boiling
at 94–95°; after remaining at rest for some time, it is spon-
taneously, and sometimes rapidly, converted into what is
called *insoluble chloral*, which is a white, opaque, porcellaneous,
hard mass, and, when heated to 180°, re-forms ordinary
chloral.

The aldol, CH_3 . $CH(OH)$. CH_2 . CHO, of Würtz also poly-
merizes readily, forming paraldol, which is a beautiful crystal-
line solid, melting at 90° (*Comptes Rendus*, lxxxiii. p. 255).
Some aldehydes are only known in the polymeric state, as
oxalic aldehyde or glyoxal*, CHO . CHO.

From analogy, this body ought to be gaseous, or at least
a very volatile liquid at the ordinary temperature :—

---

* Given the difference in volatility between the chlorides of the nega-
tive radicals and the corresponding aldehydes,

<div align="center">

CH_3 . $COCl$, b.-p. 55°, CH_3 . COH, b.-p. 21°,

</div>
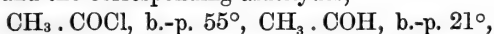
we should conclude that ordinary succinic aldehyde was a polymer :—

<div align="center">

$COCl$. CH_2 . CH_2 . $COCl$, b.-p. 190°,

COH . CH_2 . CH_2 . COH, b.-p. 201°–203°.

</div>

$$\underset{\underset{CH_3}{|}}{CHO} \quad \text{b.-p. } 21°, \qquad \underset{\underset{CH_3}{|}}{CHCl_2} \quad \text{b.-p. } 60°,$$

$$\underset{\underset{CHCl_2}{|}}{CHCl_2} \text{b.-p. } 140°, \qquad \underset{\underset{CHCl_2}{|}}{CHO} \quad \underset{\underset{CHCl_2}{|}}{CHO} \quad \text{b.-p. } 87°.$$
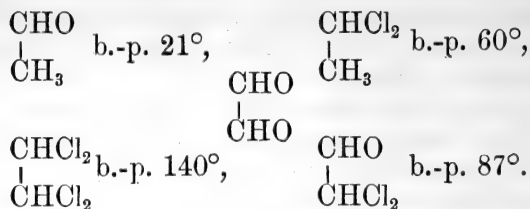
In reality, however, glyoxal is only known as a non-volatile viscous mass. It is unnecessary to extend these examples, for the same facts are illustrated in various degrees by all the members of this group (see Bruylants, 'On the Polymerization of the Aldehydes,' *Inaug. Diss.*, Louvain, 1875). The self-additive power of methylene oxide, which is so evident in its mono-derivatives, the aldehydes, is less marked in its di-derivatives, the acetones. Though true polymers of acetone itself are unknown, yet those of some of its chloro-derivatives have been obtained by Grabowsky (*Ber.* viii. p. 1438).

If we compare the boiling-points of the glycollic, aldehydic, and acetonic chlorides with those of the corresponding oxides, thus:—

$CH_2 . CH_2 . O$ ... b.-p. $13°$		$CH_2Cl . CH_2Cl$ ...... b.-p. $84°$
$CH_3 . CHO$ ...... „ 21		$CH_3 . CHCl_2$ .... „ 60
$CH_3 . CH . CH_2 . O$ „ 35		$CH_3 . CHCl . CH_2Cl$ „ 96
$CH_3 . CH_2 . CHO$ „ 47		$CH_3 . CH_2 . CHCl_2$ „ 85
$CH_3 . CO . CH_3$ ... „ 56		$CH_3 . CCl_2 . CH_3$ „ 70

and if we further bear in mind the general fact that in the isomeric substituted derivatives of the paraffins, the volatility is the greater when the substitution has taken place in a chain or chains which are least hydrogenated, then we must conclude that the aldehydes and acetones are only known to us in the state of polymers, which depolymerize completely at the boiling-point. Thus, acetic aldehyde should be gaseous and more volatile than the oxide of ethylene; propionic aldehyde more volatile than oxide of propylene; and acetone more volatile than the corresponding aldehyde C_3H_6O. The real relations are, however, the reverse of these.

Actual Polymerization of the Oxides themselves.

The actual polymerization of the oxides is readily indicated by all those characters which have been long observed in the case of the special variety of oxides called by Chevreul " oxydes cuits." Certain anhydrous and pulverulent metallic oxides,

obtained by dehydration of their hydroxides at as low a temperature as possible, suddenly enter into vivid incandescence when exposed to a higher temperature, verging on redness. Their properties are thus modified both physically and chemically; they become denser, harder, and, when coloured, their colour is intensified. They show a greater resistance to the action of chemical agents than in their former condition, some even entirely resisting the action of acids and alkalies. Fe_2O_3, Cr_2O_3, ZrO_2, &c., are examples. The fact of this vivid incandescence, which is not accompanied by any alteration in the composition of the product, is the manifest proof of an energetic combination of the oxide with itself. When hydrocarbons, such as amylene, terebenthene, &c., are polymerized under the action of certain agents, such as sulphuric acid, and especially boron fluoride, a development of heat takes place which is frequently considerable. Finally, arsenic trioxide is a direct proof of accumulation in a single molecule, even in the gaseous state, of several normal molecules corresponding to the chloride. Arsenic trichloride being $AsCl_3$, the corresponding oxide ought to be As_2O_3. This is in fact the arsenical oxygenated compound which is present in the arsenites of methyl and ethyl (*Bull. Soc. Chim.* xiv. p. 101), compounds which are volatile without decomposition, and whose formulæ, as deduced from vapour-density determinations, are $(CH_3)_3AsO_3$ and $(C_2H_5)_3AsO_3$. The molecule of arsenious oxide in the gaseous state corresponds not to As_2O_3, but to $(As_2O_3)_2$ or As_4O_6, as proved by its vapour-density. It volatilizes at about 200° without fusion; and there can be no doubt that its molecule in the solid state is some multiple of its gaseous molecule As_4O_6. There is thus established between the methylenic compounds and the arsenious ethers a complete parallel. To this we shall refer again.

Various Methods of Producing the Oxides.

By Dehydration of the Hydroxides.—The various methods of obtaining the oxides from other compounds containing them as radicals also tend to show that they are polymers. Among these methods, one of the most important, on account of its generality, and also the most interesting from our particular point of view, is the dehydration of hydroxides. Under the action of heat the hydroxides, with but few exceptions, lose water, either wholly or partially. But, however this may be, the dehydration is the more complete the higher the temperature. This temperature varies according to the nature of the hydroxide. Some of the latter have only an ephemeral existence at the ordinary temperature, and are therefore more

usually represented by their anhydrides.   In addition to these general facts, it is important to observe not only the nature of the anhydrides thus obtained, but also the connection which underlies the two distinct chemical phenomena, viz. dehydration and molecular condensation.   Würtz developed this principle in one of his lectures before the Chemical Society of Paris in 1863.   The elimination of water usually depends not on one but on several molecules of the hydroxide, the residues of which become soldered together, as it were, by the atoms of oxygen ; we therefore get an accumulation of the radicals of these hydroxides in the products formed—a veritable *molecular condensation proportional to this accumulation.*   This principle applies to all hydroxides indiscriminately, not only to the normal hydroxides $R^x(OH)_x$, but to the oxyhydroxides or incomplete anhydrides $R^x O_n(OH)_{x-2n}$.   It therefore follows that the compounds formed under these conditions become more and more complex, in proportion as this dehydration itself is more or less complete.

These general facts apply to all hydroxides, both organic and mineral.   The following are illustrations from organic chemistry:—

The acid alcohols are the most interesting in this connection. The most simple, and therefore the most conclusive cases are furnished by the glycollic and lactic acids.   When heated, these compounds lose successively a half and then a whole molecule of water, forming finally glycollide and lactide.   I have shown (*Bull. Acad. Belg.* xxvii. p. 409) that lactide in the *state of vapour* ought to be represented by the formula $[(C_3H_4O)O]_2$, and not by the usual formula $(C_3H_4O)O$.   The same thing applies also to glycollide, which is nonvolatile. If we represent the radicals glycollyl (C_2H_2O) and lactyl (C_3H_4O) respectively by Gl and La, the action of heat on glycollic and lactic acids will be expressed thus*:—

$$Gl\!\!\begin{array}{c}OH\\OH\end{array}, \qquad O\!\!\begin{array}{c}Gl-OH\\Gl-OH\end{array}, \qquad O\!\!\begin{array}{c}Gl\\Gl\end{array}\!\!O,$$

$$La\!\!\begin{array}{c}OH\\OH\end{array}, \qquad O\!\!\begin{array}{c}La-OH\\La-OH\end{array}, \qquad O\!\!\begin{array}{c}La\\La\end{array}\!\!O.$$

---
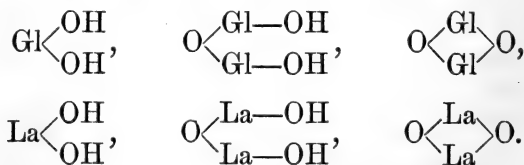
* The following considerations prove that glycollide cannot be $C_2H_2O_2$, but is really a polymer $(C_2H_2O_2)_n$.   The minimum molecule of glycollic acid is represented by $CH_2OH . COOH$, and contains therefore the tetravalent radical ($\equiv C . CH_2-$).   The corresponding chloride $CCl_3 . CH_2Cl$ is a liquid, b.-p. 102°.   Consequently the oxide, or glycoll, $O=C . CH_2 . O$, ought to be still more volatile, just as the oxide of methylene is gaseous, whilst the chloride CH_2Cl_2 is a liquid, b.-p. 40°.   In reality, however, this is not the case, for glycollide is a fixed solid.

Ethylenic hydroxide, $CH_3 . C(OH)_3$ (or acetic acid, $C_2H_4O_2 + H_2O$), when distilled, is dehydrated, and forms the corresponding oxyhydroxide (*i. e.* the common acetic acid), which is represented in the state of vapour, not by the formula $C_2H_4O_2$ or $CH_3 . CO . OH$, but by $(C_2H_4O_2)_2$ or

$$CH_3 . C(OH) . O . C(OH) . CH_3.$$
$$\underline{\qquad O \qquad}$$
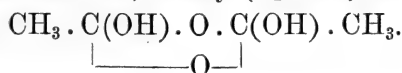
Again, the transformation on prolonged distillation at the ordinary pressure of certain polyatomic hydroxides, notably glycerol, $C_3H_5(OH)_3$, and its monochlorhydrines, $C_3H_5(OH)_2Cl$, into condensation-products by dehydration are further examples of this fact.

Returning now to the dehydration of mineral hydroxides, we have examples in the case of the acid hydroxides.

1. *Phosphoric Acid*, H_3PO_4 or $(HO_3)PO$, when heated to 200°, is converted into pyrophosphoric acid, $H_4P_2O_7$ or $(HO)_2PO . O . PO(OH)_2$. Note also, in passing, the various modifications of condensed metaphosphoric acid, discovered by Fleitmann and Henneberg.

2. *Boric Acid*, when dry and crystalline, is represented by H_3BO_3. On heating, it dehydrates progressively as follows:—

Dried at ordinary temperature	.	H_3BO_3.
„ 100°	. . . . . .	HBO_2 or $H_2B_2O_4$.
„ 160°	. . . . . .	$H_2B_4O_7$.
„ 270°	. . . . . .	$H_2B_{16}O_{25}$.

At higher temperatures there is total dehydration and formation of fused anhydride $(B_2O_3)_n$.

3. *Silicic Acid.*—Normal silicic acid, H_4SiO_4, is scarcely known as such. It no doubt forms the gelatinous silica when freshly precipitated. When heated, it exhibits progressive dehydration:—

Dried at ordinary temperature	.	H_2SiO_3 or $H_4Si_2O_6$.
„ 20°–25°	. . . . .	$H_2Si_2O_5$.
„ 60°	. . . . . .	$H_2Si_3O_7$.
„ 80°–100°	. . . .	$H_2Si_4O_9$.
„ 250°–270°	. . . .	$H_2Si_8O_{17}$.

After which, total dehydration with formation of $(SiO_2)_n$.

4. *Titanic Acid.*

Dried at ordinary temperature	.	H_4TiO_4.
„ over H_2SO_4	. . . .	H_2TiO_3 or $H_4Ti_2O_6$.
„ at 60°	. . . . . .	$H_6Ti_4O_{11}$.
„ at 100°	. . . . . .	$H_2Ti_2O_4$.

Also similarly with molybdic and stannic hydrates.

It is well to state here that I do not attach an absolute value to the formulæ attributed to a good number of these incomplete hydrates of mineral acids. It would be difficult to regard all of them as definite compounds. The fact which is in evidence, and with which alone we are at present concerned, is that with rise of temperature the dehydration goes on, and the molecular composition becomes more and more complicated by the accumulation of radicals in the oxyhydroxyl residue. Though these hydrates themselves may not always have the character of well-defined compounds, they are often represented by corresponding derivatives having all the characteristics of true chemical substances.

It is sufficient to mention Troost and Hautefeuille's oxychlorides of silicon, the numerous polysilicates, so varied in composition and often so well defined, the condensed metaphosphates, the molybdates, &c. Certain anhydrides, which are totally wanting in oxyhydroxides, are represented by well-defined salts, as in the case of chromic acid, of which the bi- and tri-chromates, $R_2Cr_2O_7$ and $R_2Cr_3O_{10}$, are well known. Metallic hydroxides also behave like the acid hydroxides, thus :—

1. *Normal Plumbous Hydroxide* should be $Pb(OH)_2$, but as ordinarily produced it is already partially dehydrated. Dried at a low temperature, it has the formula $H_2Pb_2O_3$ (Tünnermann, Schaffner, &c.) or $H_2Pb_3O_4$, in the form of minute crystalline grains (Payen). At 100° it loses all its water.

2. *Hydrates of Copper.*—Cupric hydrate, $Cu(OH)_2$, is the bluish precipitate obtained on adding very dilute alkalies to solutions of cupric salts. Heated in water, this hydroxide dehydrates partially and becomes black. It then has the following composition :—

Dried over sulphuric acid . . $H_2Cu_3O_4$ (Harms).
    „   at 100° . . . . . . $H_2Cu_6O_7$ (Rose).

Normal cuprous hydrate would have the minimum formula $Cu_2(OH)_2$. On partial dehydration it gives $H_2(Cu_2)_8O_9$ (Millon and Commaille), and $H_2(Cu_2)_4O_5$ (Mitscherlich).

3. *Hydrates of Thorium.*—One of the known hydrates, dried at 100°, corresponds to H_4ThO_4; another, obtained by a different method, and dried at the same temperature, corresponds to $H_2Th_4O_9$ (Clere).

4. *Manganic Hydrates.*—Several hydroxides, formed under various conditions, correspond to the peroxide MnO_2, and are as follows:— H_2MnO_3, $H_2Mn_2O_4$, $H_2Mn_3O_7$, $H_2Mn_4O_9$, and $H_4Mn_3O_8$. All these dehydrate, when heated, forming MnO_2.

5. *Ferric Hydrates.*—The following hydrates of ferric oxide, Fe_2O_3, are known:—

Normal hydrate,	$H_6(Fe_2)O_6$	.	.	Limonite,	$Fe_2O_3 . 3H_2O$.
,,	,, $H_4(Fe_2)O_5$	.	.	,,	$Fe_2O_3 . 2H_2O$.
,,	,, $H_2(Fe_2)O_4$	.	.	Göthite,	$Fe_2O_3 . H_2O$.
,,	,, $H_6(Fe_2)_2O_9$	.	.	Limonite,	$2Fe_2O_3 . 3H_2O$.
,,	,, $H_2(Fe_2)_2O_7$	.	.	Turgite,	$2Fe_2O_3 . H_2O$.
,,	,, $H_{10}(Fe_2)_3O_{14}$.	.		,,	$3Fe_2O_3 . 5H_2O$.

On heating, they are all dehydrated to Fe_2O_3.

The brown ochreous precipitate obtained on adding an alkali to ferric chloride is undoubtedly $Fe_2(OH)_6$, but when dried in a vacuum it has the composition $(Fe_2)_2H_6O_9$, or $2Fe_2O_3 . 3H_2O$. Heated to ebullition, it dehydrates and becomes $Fe_2H_2O_4$ or $Fe_2O_3 . H_2O$. By prolonged ebullition it can be totally dehydrated.

6. *Aluminium Hydrates.*—Aluminium solutions, on addition of ammonia in excess, give the normal hydrate $Al_2(OH)_6$ in the form of a white gelatinous precipitate. On prolonged ebullition this is partially dehydrated, like the corresponding ferric hydrate, and becomes insoluble in acids and in alkalies, like calcined alumina (Péan de St. Gilles). This new hydroxide corresponds to the formula $(HO)_2Al_2 . O . Al_2(OH)_2$, which is analogous to pyrophosphoric acid. Besides the normal hydrate $Al_2(OH)_6$, hydrargillite, there is also the mineral diaspore, $Al_2O_2(OH)_2$ or $Al_2O_3 . H_2O$, to which we shall refer hereafter.

All these oxyhydroxides, both natural and artificial, which are products of the condensation of the normal hydrates, are completely dehydrated under the action of heat, at a temperature above that at which they are formed.

Since the same causes produce the same effects, it is natural to conclude that the last phase of the dehydration is accompanied, as in those which precede it, by an analogous molecular condensation. The elimination of water having determined the accumulation of the radicals in the products to which they give rise, it would be unreasonable and illogical to suppose that an entirely different phenomenon occurred at the moment of elimination of the last molecule of water, resulting in the dislocation of these residues of condensation previously soldered together by the intermediatory oxygen.

Dehydration and condensation are intimately connected. We must conclude, therefore, that at the moment the last molecule of water is given off, not only does the previous condensation of the oxyhydroxide remain, but that, conformably to the general rule, it becomes still more accentuated.

Thus, when crystalline plumbous hydrate, $3PbO \cdot H_2O$, loses its last molecule of water under the action of heat, it is not PbO which is formed, but at least $(3PbO)_2$. When $H_2Si_8O_{17}$ becomes the anhydride, we do not get SiO_2, but at least $(Si_8O_{16})_2$. For a similar reason metaphosphoric acid cannot be HPO_3, but is at least $(HPO_3)_2$, since it is formed by dehydration of $H_4P_2O_7$.

The structure of these oxyhydroxides leads to the conclusion that they are, in effect, fragments of the normal hydroxides, $R^x(OH)_x$, linked together by atoms of oxygen, thus :—

$$
\begin{array}{ll|ll}
H_3PO_4 \ . \ . & PO(OH)_3 & H_2PbO_2 \ . \ . & Pb(OH)_2 \\
H_4P_2O_7 \ . \ . & PO(OH)_2 & H_2Pb_3O_4 \ . \ . & Pb(OH) \\
 & \quad | & & \quad | \\
 & O & & O \\
 & \quad | & & \quad | \\
 & PO(OH)_2 & & Pb \\
 & & & \quad | \\
 & & & O \\
 & & & \quad | \\
 & & & Pb(OH)
\end{array}
$$
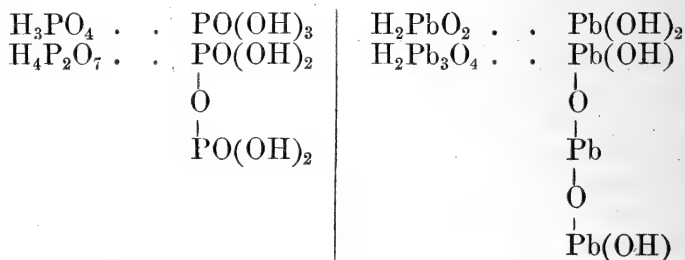
The fact of the polymerization of an oxide at the moment of dehydration of the corresponding hydroxide, is also confirmed experimentally in certain cases, thus :—The methylic and ethylic arsenites $(CH_3)_3AsO_3$ and $(C_2H_5)_3AsO_3$ are decomposed by water, and give, not arsenious acid, H_3AsO_3, but the solid anhydride, which is, even in the state of vapour, a polymer represented by As_4O_6.

The same thing also holds good with methylene oxide. Its chloracetate, $CH_2Cl \cdot O\overline{Ac}$ (Henry, *Bull. Acad. Belg.* xxxv. p. 717), its diacetate, $CH_2(O\overline{Ac})_2$, and the compounds obtained by Friedel (*Compt. Rend.* lxxxv. p. 2471) are also decomposed by water, yielding, not the hydroxide $CH_2(OH)_2$, but the solid polymerized oxide $(CH_2 : O)_x$.

The metallic oxides can be obtained from their different salts by various reactions. These general methods furnish a number of facts which tend to prove the polymeric nature of these compounds. We will examine successively in this connection the various classes of salts, such as carbonates, sulphates, &c.

Carbonates.—As a general rule most carbonates are decomposed by heat, leaving an oxide. For this reason these salts are perfectly assimilable to the hydroxides, and we may therefore confirm by their help the results previously arrived at. The chief difference is the degree of heat required.

It is important, from our point of view, to show that de-

carbonation, like dehydration, does not occur all at once, but is continuous and progressive according to the temperature. The course of this decomposition is clearly shown in particular cases, notably in the decomposition of certain insoluble carbonates in the presence of water, and at a slightly elevated temperature, and often at the moment of precipitation. The decomposition results in the formation of basic carbonates, anhydrides or hydrates, oxy- or hydroxy-carbonates, of a composition more or less complex, and in the smallest molecule of which are accumulated several molecules of metallic oxide or hydroxide. A large number of metals, *e. g.* Mg, Zn, Pb, Cu, Bi, Hg, Al, Cr, Fe, Co, Ni, &c., furnish remarkable examples of this general fact. These insoluble basic carbonates are usually obtained by precipitation with soluble carbonates, either from hot or cold metallic solutions. The composition of these precipitates for the same metal, frequently varies between more or less wide limits, depending on the special circumstances under which the precipitation has taken place. It is evident that these various compounds cannot all be considered as well defined. There are some however, the chemical individuality of which has been well established, and a number of these, either natural or artificial, are capable of assuming the crystalline state. The following are examples :—

a. **Mg** . . . $3CO_2 . 4MgO + 4H_2O.$
$4CO_2 . 5MgO + 5H_2O.$ Magnesia alba.
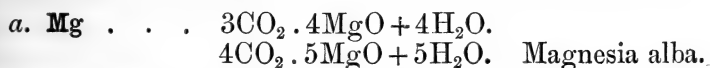
b. **Zn**. Composition very varied.

$ZnCO_3 . Zn(OH)_2 + 2H_2O.$
$2ZnCO_3 . Zn(OH)_2.$
$2ZnCO_3 . 3Zn(OH)_2.$ Crystalline.
$4ZnCO_3 . 7Zn(OH)_2 + H_2O$ (the preceding dried at 100°).
$3ZnCO_3 . 5Zn(OH)_2 + H_2O.$
$ZnCO_3 . 2Zn(OH)_2 + H_2O$ (natural).
$ZnCO_3 . 3ZnO + 2H_2O.$
$ZnCO_3 . 7ZnO + 2H_2O.$
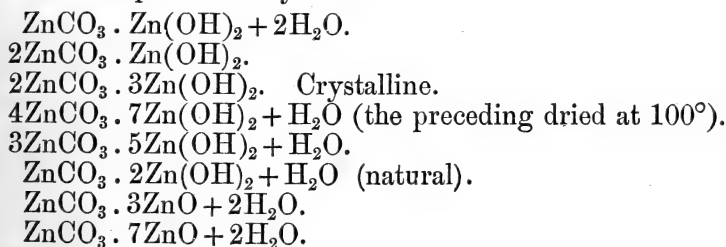
c. **Pb**. The following, according to H. Rose, represent the composition of the hydrocarbonates of lead formed under definite conditions :—

$6PbCO_3 . Pb(OH)_2 + H_2O$ $\left\{ \begin{array}{l} \text{by mixing cold and concen-} \\ \text{trated solutions of sodium} \\ \text{carbonate and lead nitrate in} \\ \text{equivalent quantities.} \end{array} \right.$

$5PbCO_3 . Pb(OH)_2.$ . . ditto, but dilute and cold.
$3PbCO_3 . Pb(OH)_2.$ . . ditto, but dilute and boiling.
$2PbCO_3 . Pb(OH)_2.$ . . ditto, but with excess of alkaline carbonate.
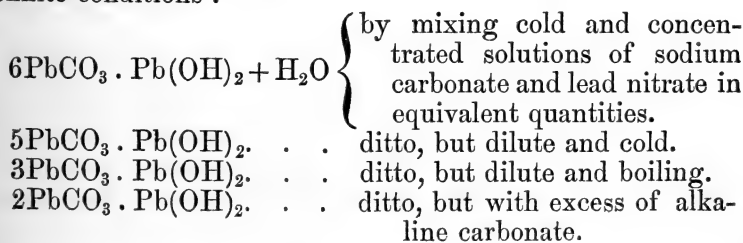
d. **Cu.** Two basic hydrocarbonates of copper are natural compounds, viz. malachite and azurite, but both may be produced artificially.

$$CuCO_3 . CuO . 2H_2O.$$
$$CuCO_3 . CuO . H_2O \quad \text{(Malachite)}.$$
$$2CuCO_3 . CuO . H_2O \quad \text{(Azurite)}.$$

e. **Co** and **Ni.**

$2CoCO_3 . 2Co(OH)_2 + 5H_2O$ $\left\{ \begin{array}{l} \text{by precipitating a cobalt salt} \\ \quad \text{by alkali carbonate in the} \\ \quad \text{cold.} \end{array} \right.$

$2CoCO_3 . 3Co(OH)_2 + H_2O$ $\left\{ \begin{array}{l} \text{the preceding precipitate} \\ \quad \text{after washing at a boiling} \\ \quad \text{heat.} \end{array} \right.$

$CoCO_3 . 3Co(OH)_2 + H_2O$ $\left\{ \begin{array}{l} \text{the same boiled with carbo-} \\ \quad \text{nate of soda, \&c.} \end{array} \right.$

$2NiCO_3 . 3Ni(OH)_2 + 2H_2O$ $\left\{ \begin{array}{l} \text{by precipitating nickel sul-} \\ \quad \text{phate with sodium carbo-} \\ \quad \text{nate in the cold.} \end{array} \right.$

As a general rule these precipitates become more and more basic as the temperature of precipitation is higher, and, like the corresponding hydrates, they become decarbonated and dehydrated under a more or less intense heat. The cause which determines the molecular complexity of these compounds, the accumulation of the metallic radicals in the same product, leads as a final result to a true oxide. The production of a simple monometallic oxide RO_x by the action of heat, would consequently compel us to assume, that at a given moment an effect was produced quite contrary to all that had preceded it.

Nitrates, Sulphates, and Chlorides.—The following phenomena are quite analogous to that which we have just examined. We have seen that certain carbonates, formed in the presence of water, are partially decomposed by the latter, with the formation of a hydroxide, and the final production of a basic hydrocarbonate, the radical CO_3 being replaced by HO. The nitrates, sulphates, and chlorides of certain metals, notably those whose oxides are feeble bases, undergo a similar change in the presence of water. A salt originally neutral in composition is first converted into a basic salt, and finally, under the action of heat, in the presence of a large quantity of water (either alone or slightly alkaline), into a true oxide. Thus :—

Mercuric Nitrate $Hg(NO_3)_2$, under the action of cold water, gives a basic trimercuric nitrate $Hg(NO_3)_2 . 2HgO$, which

is a yellow salt, known as *turbith nitreux*. By prolonged treatment with water this salt becomes more and more basic. Kane has described a salt having the composition $Hg(NO_3)_2$. $5HgO$. Finally it gives mercuric oxide. Nitrate of bismuth behaves in a similar manner. A large quantity of water, hot or cold, converts *mercuric sulphate*, $HgSO_4$, into trimercuric sulphate, $HgSO_4$. $2HgO$, which, in the presence of an alkaline solution, finally becomes mercuric oxide. The solution of *oxide of antimony* in fuming sulphuric acid yields, according to Peligot, the crystalline salt Sb_2O_3 . $2SO_3$. The latter in the presence of water gives the basic salt H_2SO_4 . $2Sb_2O_3$, which completely decomposes in the presence of a large quantity of water into oxide of antimony. *Antimony trichloride*, $SbCl_3$, gives, when treated with water, white precipitates of oxychlorides, which are finally converted into the oxide. One of these compounds is crystalline, and has the formula $5Sb_2O_3$. $2SbCl_3$. It is well known with what facility oxide and chloride of mercury combine to form oxychlorides $(HgO)_x$. $(HgCl_2)_y$. These can be obtained in different ways, and are of very varied composition. Several of them are crystalline, one of the latter being $6HgO$. $HgCl_2$. They are all converted into mercuric oxide in alkaline solution.

It is only natural to suppose that, when these various basic compounds are converted, either by the action of water alone, or in the presence of an alkali, into the oxide, with the total elimination of the acid radical and its replacement by oxygen, the bonds, which hold together the several radicals or atoms of the metal in one and the same molecule, remain throughout. The action of the water having originally determined them, it would be illogical to suppose that at a particular moment they cease to act.

Acid Anhydrides.—The same reasoning may be applied to anhydro-compounds produced by the action of strong acids on their salts, and especially on their acid anhydrides, as in the case of the chromates.

Chromic anhydride, CrO_3, forms three series of salts :—

Monochromates	.	K_2CrO_4 or K_2O . CrO_3.
Dichromates	. .	$K_2Cr_2O_7$ or K_2O . $2CrO_3$.
Trichromates	. .	$K_2Cr_3O_{10}$ or K_2O . $3CrO_3$.

Under the action of an acid, such as sulphuric, the monochromate is converted successively into the di- and tri-chromates, and finally into the anhydride. The latter ought, therefore, to be represented by some multiple of CrO_3.

Finally, we find a direct proof of this polymerization in the decomposition of the arsenites by acids. Among these salts

there are some which contain several molecules of As_2O_3 in their molecule, such as :—

$$K_2O \cdot (As_2O_3)_2 \cdot H_2O.$$
$$K_2O \cdot (As_2O_3)_2.$$
$$2K_2O \cdot (As_2O_3)_3 \cdot 3H_2O.$$
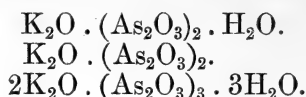
All these salts, under the action of acids, give arsenious anhydride, which, even in the state of vapour, is represented by $(As_2O_3)_2$. Here we have a proof of the accumulation of radicals, which exists in the primitive salt, remaining in the expelled oxide.

Comparative Density of Oxides.

A comparison of the specific gravities of the metallic oxides with those of other compounds, containing the same radical, furnishes a new argument for the polymerization of the oxides.

The specific gravity of a solid body doubtless depends in a great measure on the state of aggregation, and is also ultimately connected with the composition of the body and the size of the molecular weight. This connection becomes evident in the case of isomorphous solid bodies, which differ by elements of which the atomic weights are very far apart as to their numeric value.

The density, then, is to a certain degree a function of the molecular weight. If the oxides corresponding to the normal hydrates, less water, be represented by

$$R^x(OH)_x = R^xO_{\frac{x}{2}} - \frac{x}{2}H_2O,$$
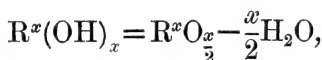
it follows that, having a smaller molecular weight than the hydroxides, their density in the solid state should also be less than that of the latter. This is in fact the relation which is observed between the glycols and their anhydrides, which latter are the oxides of the radicals C_nH_{2n}, thus :—

	Molecular weight.	Density.
$C_2H_4(OH)_2$	62	1·126 at 0°
$C_2H_4 : O$	45	0·898 ,,
$C_3H_6(OH)_2$	76	1·051 ,,
$C_3H_6 : O$	59	0·859 ,,
$C_5H_{10}(OH)_2$ ...	104	0·987 ,,
$C_5H_{10} : O$	87	0·824 ,,

A difference of an exactly inverse order exists between the

metallic hydrates and their anhydrides, the latter having generally a greater density. The density gradually and successively increases as the hydrate loses its water, until it attains its maximum in the anhydrides or oxides themselves. For example :—

		Molecular weight.	Density.
$Mg(OH)_2$	Brucite	58	2·34
MgO	Periclase	40	3·65
$Zn(OH)_2$	Crystallized	99	2·677
Zn	Crystallized	81	6·00 about
	Amorphous	81	5·60
$Mn_2O_3 . H_2O$	Acerdese	176	4·325
Mn_2O_3	Braunite	158	4·750
$B(OH)_3$	Crystallized	62	1·48
B_2O_3	Fused	70	1·83
$2Fe_2O_3 . 3H_2O$	Limonite	374	3·6 to 4·0
$Fe_2O_3 . H_2O$	Göthite	178	4·0 to 4·4
Fe_2O_3	Oligiste	160	5·24 to 5·28
	Calcined	160	5·04 to 5·17
$Al_2O_3 . 3H_2O$	Hydrargillite	157	2·35
$Al_2O_3 . H_2O$	Diaspore	121	3·45
Al_2O_3	Corundum	103	4·00

It should be noticed that a marked difference in density is observed in the case of substances which are known to be polymeric, thus :—

		Molecular weight.	Density.
C_2H_4O	Acetic aldehyde	44	0·801 at 0°.
	Ethylene oxide	44	0·898 ,,
$(C_2H_4O)_2$	Diethylene oxide	88	1·048 ,,
$(C_2H_4O)_3$	Paraldehyde	132	0·998 at 15°.
C_5H_8	Isopropylacetylene	68	0·652 at 11°.
$C_{10}H_{16}$	Terebenthene	136	0·8767 at 0°.
$C_{20}H_{32}$	Colophene	272	0·94 at 9°.
C_5H_{10}	Amylene	70	0·663 at 0°.
$C_{10}H_{20}$	Diamylene	140	0·777 ,,
$C_{15}H_{30}$	Triamylene	210	0·8139 ,,

Relations similar to those which are observed between the hydroxides and the oxides also exist between the latter and the chlorides. The densities of the oxides of the radicals C_nH_{2n} are notably less than those of the corresponding chlorides, and this difference is in some degree similar to that between the molecular weights of these compounds, thus :—

		Molecular weight.	Density.
C_2H_4O ...... {	Acetic aldehyde	44	0·801 at 0°.
	Ethylene oxide	„	0·898 „
$C_2H_4Cl_2$ ... {	Ethylene chloride	99	1·256 at 12°.
	Ethylidene chloride	„	1·189 at 4°·3.
C_3H_6O ...... {	Propionic aldehyde	58	0·8074 at 21°.
	Propylene oxide...............	„	0·859 at 0°.
	Acetone	„	0·814 „
$C_3H_6Cl_2$ ... {	Aldehydic chloride............	113	1·143 at 10°.
	Propylene chloride	„	1·1584 at 0°.
	Acetonic chloride	„	1·117 at 0°.
	Normal propylene chloride	„	1·201 at 15°.
$C_5H_{10}O$ ... {	Valeric aldehyde	86	0·822 at 0°.
	Amylene oxide	„	0·824 „
	Various Ketones...............	86	{ 0·8132 at 13°. 0·8099 „ 0·813 at 20°.
$C_5H_{10}Cl_2$ ... {	Aldehydic chloride	141	1·05 at 24°.
	Amylene chloride	„	1·058 at 9°.
	Acetonic chloride	„	1·06 at 5°.

Now the difference between the density of the chlorides and oxides of the metals in general is exactly the inverse of the above, for the density of the oxides is notably greater than that of the apparently analogous chlorides, thus :—

		Molecular weight.	Density.
{ $CaCl_2$		111	2·16 to 2·205.
{ CaO		56	3·08 to 3·20.
{ $ZnCl_2$		136	2·753 (Bödeker).
{ ZnO		81	5·7334 (Karsten).
{ $CdCl_2$		183	3·625 (Bödeker).
{ CdO...........		128	6·9502 (Karsten).
{ $PbCl_2$		278	5·802 (Karsten).
{ PbO...........		223	9·2 to 9·5.
{ $PbCl_2+PbO$	Mendipite	491	7·00 to 7·10 (Berzelius).
{ $PbCl_2+2PbO$	Matlockite........	724	7·21 (Rammelsberg).
{ Hg_2Cl_2.........		471	6·56 (Schiff), 7·14 (Boullay).
{ Hg_2O		416	{ 8·95 (Karsten). 10·69 (Herapath).
{ $HgCl_2$		271	5·4 (Karsten).
{ HgO...........	(Crystallized) ...	216	11·29 (Roger & Dumas).
{ Cu_2Cl_2	(Fused)	198	3·677 (Karsten).
{ Cu_2O		143	5·749 to 6·093 .
{ Ag_2Cl_2	Fused	287	5·59 (Schröder).
{ Ag_2O		232	{ 7·143 (Herapath). 8·2558 (Karsten).
{ $NiCl_2$		129·75	2·52 (Schiff).
{ NiO		74·75	6·398 (Bergmann).

A difference of the same kind exists between the oxides and the corresponding carbonates, thus :—

{ MgO ...	Periclase	3·65
{ MgCO₃ .	Giobertite	2·99 to 3·15
{ ZnO......	Crystallized	6·00
{ ZnCO₃...	Smithsonite	4·3 to 4·45
{ CaO......	....	3·08 to 3·2
{ CaCO₃ ..	Calcspar	2·7
	Arragonite	2·9
{ SrO	....	4·61
{ SrCO₃ ...	Strontianite	3·6
{ PbO......	....	9·2 to 9·5
{ PbCO₃...	Cerusite...............	6·57
{ BaO......	....	5·4
{ BaCO₃...	Witherite	4·28

The great difference observed between the density of certain oxides and that of their basic anhydrous salts is equally worthy of note, thus:—

	Molecular weight.	Density.
HgO . . .	216	10·69
(HgO)₃SO₃ .	728	6·444

A study of the oxides, from both a physical and chemical point of view, leads, therefore, to the general conclusion, that *for the most part the oxides cannot be compared with the chlorides; that the true oxides which are really comparable with the chlorides are unknown; and that we possess only polymers thereof* $(RO_x)_n$.

Value of the Coefficient of Polymerization.

What, now, is the true value of the coefficient n of polymerization? What is the real molecular formula of these polymeric oxides? These questions are doubtless of great interest, but it should be stated at once that it is absolutely impossible to give an exact answer. I do not know of any fact which would allow us to assign an absolute value to the coefficient n of polymerization, for we are in exactly the same position in respect to the metallic oxides as we are in the case of the solid polymeric ones of organic chemistry, *e. g.* methylene oxide, metaldehyde, &c. So far as facts will permit of a conclusion, we may affirm that *in most cases this number is very high, although different for different oxides.* The molecular weight of most oxides should therefore be considerable. This conclusion results from a consideration of certain facts previously referred to, and to which it will be necessary to return for a moment.

Oxygen is an element endowed in reality, in spite of appearances to the contrary, with great power of volatilization. It forms oxides which are gaseous, or at least very volatile, with elements which are relatively but little volatile, as sulphur; or which are even entirely fixed, as carbon and osmium. To these normal oxides, which are regular at least in their physical properties, there correspond chlorides which are notably less volatile, as in the case of those of carbon :—

$$CO_2 \text{ gaseous, b.-p.} -78.$$
$$CCl_4 \text{ liquid, b.-p.} +76.$$

That being so, it may be affirmed that many of the regular metallic oxides which correspond to the chlorides should be gaseous at the ordinary temperature, or at least very volatile. This should be especially true of SiO_2, Al_2O_3, &c.; for $SiCl_4$ is a liquid boiling at $58°$, and Al_2Cl_6 a solid volatile below $100°$. In reality, however, these oxides, which I regard as polymers, $(SiO_2)_n$ and $(Al_2O_3)_n$, are fixed solids. Organic chemistry furnishes examples of the relationships which exist in polymers between the volatility and molecular weight, thus :—

		Molec. wt.		B.-p.	Difference.
Ethylene oxide	C_2H_4O .	44	liquid	$13°.5$	$88°.5$
Ethylene dioxide	$(C_2H_4O)_2$.	88	liquid	102	
Aldehyde	C_2H_4O .	44	liquid	21	$103°$
Paraldehyde	$(C_2H_4O)_3$.	132	liquid	124	

We thus see what is the difference in volatility between bodies of which the molecular weight in the state of gas is simple, double, or treble.

Now between a body which ought to be gaseous or very volatile, such as SiO_2, and a fixed body, such as silica really is, there is a difference which cannot be compared to that which separates (as regards volatility) ethylene oxide and aldehyde from their polymers. If silica is, as I believe, a polymer $(SiO_2)_n$, then the value of n should be considerable, and the molecular weight therefore very high. We come to the same conclusion if we consider the examples which are furnished by the relative densities of the chlorides and oxides of the radicals C_nH_{2n} and those of their polymers. As already remarked above, the density of the chlorides is higher than that of the corresponding oxides, whereas the densities of the polymers of the latter rise, approaching those of the chlorides, and even going beyond. The densities of the metallic oxides are often considerably greater than those of the chlorides. If we

bear in mind the small difference which exists between the density of the oxides $C_nH_{2n}O$ and that of their polymers $(C_nH_{2n}O)_2$ or $(C_nH_{2n}O)_3$, we are led to conclude that the coefficient n of polymerization of the metallic oxides must be very high, in order to raise the density of an oxide to nearly double that of the corresponding chloride, as is frequently the case.

Doubtless the molecular condensation is different with different metallic oxides. *A priori* we should expect it to be so. This is proved by the fact that the difference between the fusibility, volatility, density, &c. of the oxides and the corresponding chlorides is very different in the several cases.

This condensation appears to attain its maximum in certain fixed and very infusible oxides, such as silica and alumina &c., the corresponding chlorides being eminently volatile. This enormous condensation of their molecules may possibly be the cause of the greater resistance which they offer to the action of chemical agents, more especially to simple chemical agents such as H, C, Cl, S, &c.

Origin and Mechanism of the Polymerization of the Oxides.

What is the origin, or, rather, what is the mechanism, of this molecular condensation which is so general in the oxides, and yet so absent in the chlorides? The diverse chemical nature of the two elements accounts for the different molecular behaviour of their compounds.

Chlorine is essentially a *monovalent* element, whilst oxygen is *divalent*. The result of this quality in oxygen is the possibility of its uniting by its two affinities with two polyvalent radicals.

From the atomic and molecular point of view, polymerization consists essentially in a simple change in which each atom of oxygen becomes united to two different atoms of the radical belonging to different molecules, and maintains them permanently together as a whole. The conversion of acetic aldehyde into its triple polymer, paraldehyde, is an interesting example of this atomic migration :—

$$CH_3 . CH—O—CH . CH_3$$

$CH_3 . CH : O$ becomes
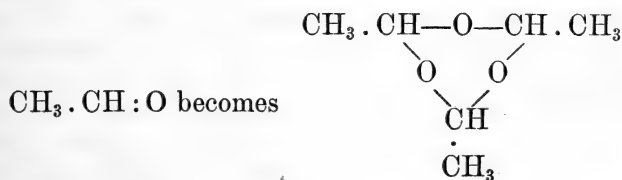
Similar facts occur, and in a similar manner, in the case of the metallic oxides, thus :—

$$H_2Pb''_3O_4 \qquad Hg''_4(NO_3)_2O_3 \qquad Hg''_4(SO_4)O_3$$
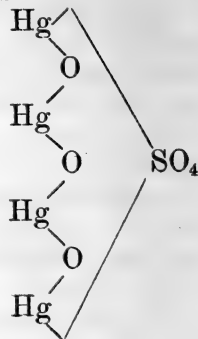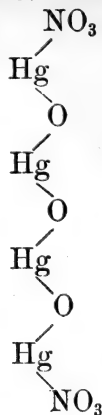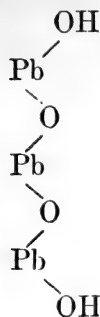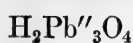
The corresponding polymeric oxides $(PbO)_n$ and $(HgO)_n$ being probably represented by analogous formulæ :—
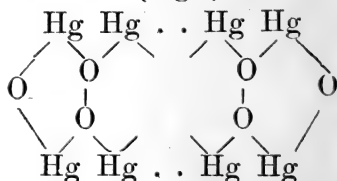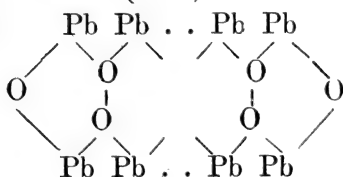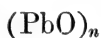
There is thus formed a kind of closed chain of polyvalent radicals alternating with n atoms of oxygen. It is thus seen that the number of atoms of the radical R accumulated in such a complex molecule may be considerable, and is theoretically illimitable. Similar groupings cannot occur in the case of the chlorides, on account of the nature of chlorine, which is a monovalent element, and consequently incapable of uniting directly with two other distinct atoms. All molecular condensation thus disappears, when in a polymeric oxide the oxygen is replaced by chlorine, as in the case of $(As_2O_3)_2$, which, under the action of chlorine, is converted into $AsCl_3$. Also, as in the case of the polymers $(C_nH_{2n}O)_x$, more especially those of aldehydes, which are converted by PCl_5 into the chlorides $C_nH_{2n}Cl_2$, identical with those furnished by the oxides $(C_nH_{2n}O)$ themselves.

Heat of Formation of the Oxides.

The combination of a body with itself, or the act of polymerization, is accompanied by the development of heat, as

with every combination of heterogeneous bodies ; and this dis-
engagement of heat may sometimes be considerable, as in the
case of the *internal* combustion (*spontaneous* in the com-
plete sense of the word), which certain metallic oxides
undergo on heating (*oxydes cuits* of Chevreul).

The quantity of heat disengaged on the formation of an
oxide RO_x in the direct way has a double origin, viz. the heat
of combination of the elements and the heat of polymeriza-
tion ; so that the direct formation of a chloride is not at all
comparable with that of an oxide. A comparison, therefore,
of the phenomena of combination, from the physical point of
view, shows that the heat evolved is an absolute measure of
the difference of the affinities between the elements of the
compound. That being so, we should conclude that the dif-
ference between the affinity of oxygen and chlorine for the
metals is in reality greater than the thermal phenomena, as
determined directly, would lead us to assume.

Action of Heat on the Oxides—their Classification.

The oxides may be divided into various groups, according
to the changes which they undergo on heating.

A. *Normal or Regular Oxides*, which correspond molecu-
larly to the chlorides. These oxides are few in number, *e. g.*
SO_2, CO_2, NO, N_2O, CO, &c.

B. *Polymerized Oxides,* the molecules of which are made
up of *n* molecules of the normal oxide united together. This
group includes most oxides, and may be divided into several
classes according to the action of heat thereon ; viz. :—

(1) *Volatile oxides, which are totally depolymerized on heat-
ing, and in the state of vapour are converted into the normal
oxide.* The number of these oxides is limited, and they are of
two kinds :—

   (a) *Oxides which are completely depolymerized on volatiliza-
tion, yielding a vapour of normal density,* e. g. SO_3,
OsO_4, and probably RuO_4 ; also various organic oxides,
such as methylene oxide $(CH_2O)_n$, metaldehyde
$(CH_3.CHO)_n$, and aldehydes and acetones in general.
On condensation the original polymeric oxides are
re-formed.

   (b) *Oxides which are depolymerized very imperfectly at the
moment of volatilization, and only completed progres-
sively as the temperature rises.* The vapour-density of
these bodies, therefore, gradually diminishes with in-
crease in temperature up to a certain point, beyond
which it becomes constant, and corresponds to that of
the normal oxide, *e. g.* N_2O_4, fatty acids, and paral-

dehyde. The vapour-density of the last corresponds to $(C_2H_4O)_3$ at low temperatures, and at higher temperatures to (C_2H_4O), *i. e.* the normal aldehyde.

(2) *Volatile oxides, which are only depolymerized imperfectly, at least at the temperatures to which they have been subjected*; *e. g.* $(As_2O_3)_n$, the gaseous molecule of which is $(As_2O_3)_2$.[*]

Lactide, or the dioxide of the radical $C_3H_4^{iv}$ (or $CH_3 . CH . C \equiv$),

is perfectly analogous to arsenious oxide, its molecule in the state of vapour corresponding to $(C_3H_4O_2)_2$. Ethylene dioxide $(C_2H_4O)_n$ probably belongs to this class, as in the state of vapour its molecule $= (C_2H_4O)_2$.

(3) *Oxides which are not capable of depolymerization.* Most inorganic oxides belong to this group; also the oxides of certain organic radicals.

They are of two kinds :—

(a) *Oxides which are absolutely indepolymerizable and fixed*, as in the case of many metallic oxides which are not decomposed by heat; *e. g.* SiO_2, B_2O_3, SnO_2, ZnO, MgO, Fe_2O_3, Cr_2O_3, Al_2O_3, PbO, CuO, Cu_2O, &c.

(b) *Oxides which are indepolymerizable, because on heating they are decomposed either into their elements or into new compounds*, as in the case of several metallic oxides; *e. g.* HgO, Ag_2O, Hg_2O, CrO_3, MnO_2, &c., and also of certain organic oxides, as glycollide $(C_2H_2O_2)_n$, which carbonizes on heating.

The above classification is conveniently represented in the following table (p. 113).

It follows from all these facts and considerations that there are large and important lacunæ in the series of oxygenated compounds of Mineral Chemistry. Shall we ever be able to obtain the whole series of normal oxides, of which we have at present so few examples? I know not. But to produce them we should doubtless have to work under conditions totally different from those which are usually employed. Our actual methods of preparation are precisely those under which these unknown bodies polymerize, and thus escape us. If it be rash to hope to obtain these bodies in the near future, it would be still more so to say that their discovery was impossible. This word is profoundly repugnant to our tendencies and scientific habits. When we measure the progress of science since the commencement of the century in a domain so vast as Chemistry, there are many reasons for not being discouraged.

[*] Arsenious oxide volatilizes, as is well known, at about 200° without melting. This temperature is not the boiling-point properly so called, but is really the temperature of depolymerization of the molecule $(As_2O_3)_n$ into $(As_2O_3)_2$.

Normal oxides, not polymerized .... CO, CO₂, SO₂, N₂O, NO

Polymerized oxides ...
- Volatile and depolymerizable ...
  - Totally .... { At the temperature of ebullition or of volatilization ... } SO₃, OsO₄, (CH₂O)ₙ, &c.
  - Incompletely ..... { Imperfectly depolymerized on ebullition, but depolymerized on superheating the vapour } N₂O₄, paraldehyde &c.
  - As₂O₃; C₃H₄O₂; (C₂H₄O)₂.
- Indepolymerizable ...
  - Undecomposable and fixed .... SiO₂, SnO₂, Al₂O₃, Cu₂O, &c.
  - Decomposable ...
    - Totally, into their elements ... Ag₂O ; HgO ; Hg₂O, &c.
    - Partially, into lower oxides } Fe₂O₃, CrO₃, MnO₂, &c.

<center>APPENDIX.</center>

Dehydration and Condensation of the Hydroxides by Heat.

It has been already stated that the hydroxides, under the action of a gradually increasing temperature, undergo a progressive dehydration, whilst at the same time their molecules become more and more condensed by the accumulation of the residual oxyhydroxides of the radical of the primitive compound. What is the cause of this general fact? This phenomenon is analogous, both in appearance and result, to that of *direct etherification*, *i. e.* to the action of an acid on an alcohol. In fact, etherification is an example of the production of an anhydrous oxide from its hydroxide. The most simple case is that in which we can follow step by step the work of dehydration, as with ordinary lactic acid.

Lactic acid, $C_3H_6O_3$, is the dihydroxide of the radical lactyl, C_3H_4O, which we may represent by La. On heating, lactic acid gives successively two anhydrides, the so-called lactic anhydride,

$$2C_3H_6O_3 - H_2O = HO . La . O . La . OH,$$

and lactide,

$$2C_3H_6O_3 - 2H_2O = La . O . La . O.$$
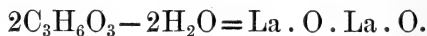
The dehydration thus takes place in two steps, and requires *at least* two molecules of acid—a fact which is easily understood from the usual formula of lactic acid,

$$CH_3 . CH(OH) . COOH.$$

The two hydroxyl groups are not equivalent; the one is acid and the other alcoholic; so that the action of heat on lactic acid is really the action of an acid on an alcohol, which mutually and successively undergo etherification, giving the so-called lactic anhydride, which is at the same time an acid, an alcohol, and an ether,

$$CH_3 . CH(OH) . CO . O . CH . COOH,$$
$$CH_3$$
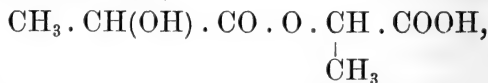
and which furnishes lactide,

$$CH_3$$
$$CH_3 . CH . CO . O . CH . CO . O,$$
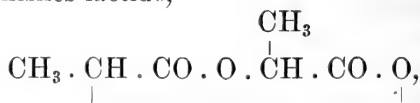
which is only but doubly an ether. If the radical lactyl were known only *en bloc*, the reason of this difference in the nature of these hydroxyls would totally escape us.

The molecule of lactide, which in the state of vapour is $(C_3H_4O_2)_2$, ought in its natural state to be still more complex. The boiling-point of this substance is really the temperature at which the grouping $(C_3H_4O_2)_{2n}$ becomes $(C_3H_4O_2)_2$. This is the logical conclusion from the molecular constitution of carboxylated acids. The molecule of acetic acid must be at least
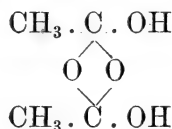
$$CH_3 . C . OH$$
$$O \quad O$$
$$CH_3 . C . OH$$

The formula $CH_3 . COOH$, commonly attributed to this acid, only represents the product of the simplification of its molecule under the action of a high temperature. That being so, the molecule of lactic acid should be at least

$$CH_3$$
$$HO . CH . C . OH$$
$$O \quad O$$
$$HO . CH . C . OH$$
$$CH_3$$
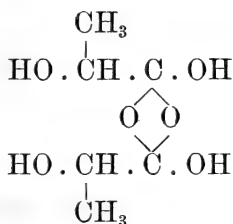
In the formation of dilactic acid and of lactide, two of such molecules act on one another, and consequently the molecule of lactide ought to be *at least* $[(C_3H_4O_2)_2]_2$, *i. e.* the double of its molecule in the state of vapour. However that may be, the hydroxides of the polyvalent radicals of mineral chemistry are assimilable to the above organic hydroxides; and we may therefore reasonably conclude that the hydroxyls which they contain are of different value. This question may be answered affirmatively and with certainty in some cases, notably that of phosphoric acid. Thomsen, Berthelot, and Longuinine have shown what is the real nature of this compound.

Orthophosphoric acid, $PO(OH)_3$, is a tribasic acid, but of quite a different kind from citric acid, in so far as in the latter the three hydroxyls are perfectly equivalent, as shown by the identity of their heats of neutralization. Citric acid, as shown by its formula, is equivalent to three molecules of carbonic acid rolled into one.

$$CH_2{-}COOH$$
$$HO . C . COOH$$
$$CH_2{-}COOH$$

I 2
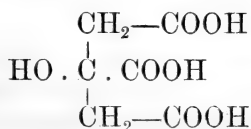
Phosphoric acid, on the contrary, is equivalent to three different acids, the heats of neutralization of the three basicities of the acid by the same metal being unequal.

$$H_3PO_4 + NaHO = 14 \cdot 68 \text{ cals.}$$
$$+ 2NaHO = 26 \cdot 33 \quad ,,$$
$$+ 3NaHO = 33 \cdot 59 \quad ,,$$
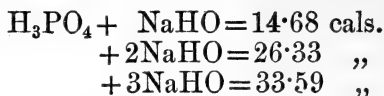
The substitution of hydrogen by sodium thus causes successively the evolution of $14 \cdot 68$, $11 \cdot 65$, and $7 \cdot 26$ cals. As regards two of its hydroxyls, orthophosphoric acid is strongly acid, though unequally, the one having an acidity similar to that of hydrochloric or nitric acid, and the other to carbonic acid ; whilst the third hydroxyl is more like that of an alcohol or phenol.

The action of heat on phosphoric acid is really the action of heat on an acid-alcohol, and ought therefore to exhibit phenomena similar to those observed in the case of lactic acid. These phenomena ought even to be more complicated, because for one molecule of $PO(OH)_3$ acting as an alcohol there is another molecule acting as an acid, and can function by one or other of its hydroxyls, which are not only acid, but unequally acid.

The formation of pyrophosphoric acid seems to be perfectly analogous to that of phosphoglyceric acid, thus :—

$$(HO)_2PO \cdot O \cdot PO(OH)_2 \quad (HO)_2 \cdot C_3H_5 \cdot O \cdot PO(OH)_2.$$
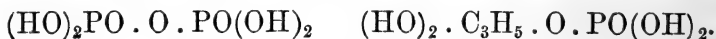
Two isomers, however, appear possible. Besides the three hydroxyls of phosphoric acid having a different chemical value, it follows that the products of the phosphoric etherification, from the partial dehydration of H_3PO_4, ought to be very numerous and complicated. Our present knowledge of the action of heat on this acid is therefore very superficial.

Can we refer the condensation of the metallic polyhydroxyls under the action of heat to the same cause—*i. e.* to a difference in the nature and value of the several hydroxyls? It seems natural and logical to do so, but it is difficult to find sufficient authority.

Phosphoryl being a multiple radical, formed of heterogeneous atoms, one can rigorously account for the fact that the three hydroxyls, which are grouped around it, are unequally placed as regards these elements, and can therefore have different values. But to conclude that the different hydroxyls attached to the same polyvalent atom, such as Si, Sn, &c., have not the same value, it would be necessary to assume that the polyvalent atoms are not identical at all

points, or at least that the various units of chemical action are not equivalent, and are therefore of unequal energy. Here we introduce one of the higher problems of chemical metaphysics. I abstain, however, from dealing with it at present.

If the condensation which certain hydroxides undergo on heating is explicable in certain cases, there are others much more numerous, which still remain without plausible explanation, and notably is this the case with the hydroxides of the elements.

On the Oxide of Methylene, $CH_2 : O$.

There is no compound more interesting than this, from the point of view of the polymerization of the metallic oxides. There is a perfect parallel between the reactions by which it may be obtained from its ethers and those by which certain oxides are prepared from their salts. Just as the arsenious ethers under the action of water give arsenious anhydride, so do the methylenic ethers, when treated with water, give methylene oxide, *i. e.* its solid polymer.

These reactions may also be compared with those which give certain metallic oxides, as Sb_2O_3, Bi_2O_3, HgO, &c., by the decomposition of their salts with an excess of water, or by weak alkaline leys. Methylene (CH_2) acts in all respects like a metal, and its oxide is strictly comparable to a metallic oxide, with this difference, that when heated it is completely depolymerized on volatilization, whereas certain oxides, as $(As_2O_3)_n$, are only imperfectly depolymerized, whilst others, such as HgO, Bi_2O_3, &c., are fixed.

In a special paper I intend to return to the oxides and chlorides of the dicarbon radicals C_2^{vi}, $C_2H_2^{iv}$, $C_2H_4^{ii}$.

XIV. *On the Thermoelectric Position of Carbon.*
By John Buchanan [*].

[Plate VIII.]

IN the very interesting paper read by Dr. J. A. Fleming before this Society on March 14, 1885, whilst discussing the question of the life of incandescent lamps, the author remarks that quite a large proportion of the carbon filaments are found to break at the negative end, that is, near the point where the current passes from carbon to platinum. It seemed to me not improbable that the negative end of the carbon might be subjected to a heating action due to the operation

---

of the " Peltier effect." The local excess of temperature thus produced might possibly account for the observed result. In any case the determination of the position of the carbon line on the thermoelectric diagram was of interest. I am not aware that this has been done before.

Result.—For the specimen of carbon I have tried, the Thomson effect is of the same sign as in copper, and about twice the value for that metal given by Prof. Tait, as quoted in Everett's " Units and Physical Constants," § 186. The thermoelectric power of carbon is given by my experiments,

$$e_c = -390 - 1{\cdot}87t \text{ C.G.S. units}, \quad . \quad . \quad . \quad (1)$$

where t denotes, as usual, the mean temperature of the junctions. The neutral point of carbon with lead is therefore about $-209°$ C.

Thermo-couple of Platinum-Carbon.—As I have mentioned, the series of experiments described below were undertaken with the object of finding the magnitude of the Peltier effect in incandescent lamps. I therefore examined specially the behaviour of a thermoelectric couple of platinum-carbon. The platinum was a piece of ordinary commercial wire procured from Messrs. Johnson and Matthey. The carbon was in the form of rods 12 millim. diam., such as are made for use in arc lamps. The direction of the current in such a couple is from platinum to carbon across the hot joint. The thermoelectric power at the mean temperature t is

$$e_{pt-c} = +566 + 3{\cdot}94t \text{ C.G.S. units}. \quad . \quad . \quad (2)$$

Due, therefore, to the " Peltier effect," heat will be generated at the negative end of the carbon filament of an incandescent lamp when the current is passing. We can now calculate what proportion the heat thus generated locally bears to the whole quantity of heat generated in the filament.

If T denote the neutral point of a thermo-couple, then the Peltier effect for the absolute temperature θ at one joint is given by

$$\pi = (K_1 - K_2)(T - \theta)\theta, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where K_1 and K_2 are the numbers that express for each material the ratio that the Thomson effect bears to the absolute temperature. (See Tait's ' Heat,' § 415.)

Hence for a platinum-carbon couple,

$$\pi = 3{\cdot}94 \ (144 + \theta)\theta. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

As a specific example, take the case of a 100-volt lamp,

with the filament at a temperature of 2400° C. We get the ratio

$$\frac{\text{Heat due to Peltier effect}}{\text{Whole heat in filament}} = \frac{3 \cdot 94 \times 2673(144 + 2400)}{100 \times 10^8},$$

$$" \quad = \frac{2 \cdot 7 \times 10^7}{10^{10}},$$

$$" \quad = \cdot 0027.$$

The local heating at the negative end of the filament is therefore only about one quarter per cent. of the whole heat. This is too small to have any appreciable influence on the life of the lamp. It does not appear therefore that the Peltier effect accounts for the giving way of the carbon-filament at one end rather than at the other. In the course of these experiments one phenomenon was forced on my attention, the details of which are given below. It seems that continuous heating alters the thermoelectric properties of carbon. This alteration must be the result of molecular change in the material. That this has any bearing on the destruction of the filament that ensues, by keeping it for a long time at a high temperature, my experiments are not extended enough to decide.

Experimental Details.

The E.M.F. at various temperatures was determined by the null method known as Poggendorff's.

The primary circuit contained a constant cell A, a graduated wire BC, and a box of resistance-coils R.

On the graduated wire were placed sliding pieces *e* and *f*, which served as the terminals of the secondary circuit. In the secondary circuit were a galvanometer G, and the thermo couple T whose E.M.F. was to be measured, and a key K.

Fig. 1.
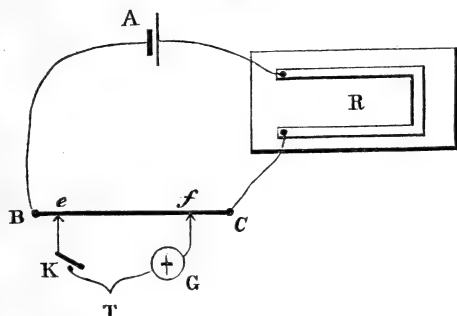
The arrangement of the apparatus used in the platinum-carbon experiments has now to be described.

Three rods of carbon of 1·2 centim. diameter, such as are manufactured for use in arc-lamps, were taken. One of these was thinned down into a conical form at the end destined to go into the hot bath. This end, and that of another rod intended to go into the cold bath, were electroplated with a thin shell of copper. To this copper shell were soldered the platinum wires, whose behaviour with the carbon I wished to examine. These two rods were then placed vertically and clamped in position with coppered ends dipping into their respective baths. The upper ends of these carbon rods were cut off square and the third rod laid horizontally, so as to form with the vertical rods the third side of a vertical rectangle.

To ensure good contact one end of this third rod was bound by a number of turns of clean iron wire to the upper end of the rod whose lower end dipped into the cold bath. The other end of this third rod rested on the top of the rod the lower end of which dipped into the hot bath. The surfaces of contact were here scraped flat and kept pressed together by a weight of 3 or 4 pounds.

The platinum wires that formed the other element of the thermo-couple were of ordinary commercial material, as was mentioned above.

The galvanometer used in the secondary circuit is a very delicate mirror instrument of about $\frac{1}{4}$ ohm resistance.

The cell used in the primary circuit as a standard was a Daniell. The graduated wire (BC in fig. 1) was of German silver.

The baths, both hot and cold, were oil-baths.

The ends of the platinum wires of the thermo-couple that were exterior to the baths were joined by binding-screws to copper wires. These joints were insulated from one another by several layers of calico, and then tightly wrapped up together. Thus in the secondary circuit the only exposed contacts of dissimilar conductors were those of the copper wires joined up with the brass binding-screws of the key, of the galvanometer, and of the sliding piece on the graduated wire. During the experiment, care was taken to screen these exposed contacts as much as possible from external radiation. Moreover, all the apparatus was set up the night before, so that on the days of the experiments no metal joints whatever in the secondary circuit were touched by hand.

Some preliminary experiments I had made showed the necessity for adopting the arrangements just described. The results of these preliminary trials exhibited very curious irregularities, not altogether got rid of even by those latest

arrangements. By using the precautions detailed above, I ensured, however, that the place of any disturbances that might come into play should be located with certainty in the thermo-joints under examination.

The proper amount of resistance to be inserted in the primary circuit having been determined beforehand, the primary circuit was closed. The current was allowed to flow during the whole time the experiment lasted. The temperature of the hot bath was raised very slowly up to the highest point reached; then as slowly lowered again. Frequent readings of the thermometers in the hot and cold baths were taken. Simultaneously were noted the positions of the movable sliders on the graduated wire, for which no deflection was shown by the galvanometer on depressing the key in the secondary circuit.

When a temperature reading was intended to be taken, the temperature was kept as steady as possible for $\frac{1}{4}$ to $\frac{1}{2}$ a minute, accompanied with constant stirring of the hot bath. In this way a series of corresponding readings of temperature and of distances on the graduated wire were obtained. The results were plotted out, taking centimetres of the graduated wire as ordinates, and temperatures of the hot bath as abscissæ. A regular curve was then drawn amongst the points thus obtained, so as to give as nearly as could be judged the mean of the observations. The curves A, B, C (Plate VIII.) were obtained in this way. The scales for these curves are not quite the same. Details are given below. The curves A and B were obtained on successive days.

The want of regularity in the individual readings, after all the precautions taken, I considered could only be due to the properties of the carbon. Partly to satisfy myself that no essential precaution had been overlooked, however, and partly to test an idea I formed as to the cause of the irregularities, the apparatus was set up again about a month later. Curve C gives the results of the observations. The heating of the hot joint gave the curve to the left hand ; the subsequent cooling gave the right-hand curve. These curves have not a point of intersection at their upper ends shown in the diagram (Plate VIII.), because the temperature was intentionally raised to a point higher than that for which a reading on the graduated wire could be obtained, before cooling down was begun.

Now, as $4\frac{1}{2}$ hours were given to the observations, the heating and cooling took place very slowly indeed. And as a stirrer was kept almost continuously in operation in the hot bath, the lagging of the thermometer behind the thermo-joint must have been very small. I believe that the dif-

ference between the curves obtained by heating and by cooling is partly due to change taking place in the properties of the carbon as the temperature changes. Bearing on this there is an observation I made. Having calculated the neutral point of a carbon-iron couple as about $+208°$ C., a glycerine bath was used to verify this result. Having raised the temperature to about $290°$ C. and cooled again to $220°$ C. several times, I found the E.M.F. of the carbon-iron couple rose gradually, until at the time of stopping the experiment the maximum E.M.F. had increased by more than 50 per cent. As is well known, a thermo-couple reaches a maximum E.M.F. when the temperature of one joint is that of the "neutral point." It was this maximum that was found to increase with the time during which heat was applied.

The conclusion is, that the thermoelectric properties of carbon alter with temperature. Principally for this reason I did not deem it of utility to begin a new series of observations, and by "loading" the hot joint with metal try to decrease the irregularities in the readings like those in curves A and B. Moreover, the results calculated from these curves agree as well as could be expected. Here are the details:—

Curve A.

Assuming the equation to the curve as

$$y = K(x-a)\left(T - \frac{x+a}{2}\right),$$

I find that $\qquad T = -147°$ C., $K = 0.00470$

satisfy best the observations as represented by the curve A.

$\qquad\qquad x =$ temperature of hot bath,
$\qquad\qquad a = \qquad\quad$ „ $\qquad$ cold bath,
$\qquad\qquad T =$ neutral point.

The agreement of calculated and observed values of y is exhibited by Table I.; these values, it will be recollected, represent centimetres of the bridge-wire. To calculate the E.M.F. of a carbon-platinum thermo-couple as given by curve A, we have the following data:—

Resistance of primary circuit . . . . . $= 303.6$ ohms.
Observed E.M.F. of Daniell used . . . . $= 1.03$ volt.
Resistance of 1 centim. of the graduated wire $= .00246$ ohm.

Denoting the E.M.F. required by E_A, we get

$$E_A = .00470 \times 1.03 \times 10^8 \frac{.00246}{303.6}(x-a)\left(147 + \frac{x+a}{2}\right),$$

$$\therefore \quad E_A = 3.92(x-a)\left(147 + \frac{x+a}{2}\right) \text{ C.G.S. units.}$$

Hence the thermoelectric power of the couple is
$$e_A = +577 + 3·92 \times t \text{ C.G.S. units,}$$
t denoting the mean temperature of the joints. The direction of the current would be from Pt to C across the hot joint.

Curve B.

Taking an equation to the curve of the same form as that just used, $T = -140°$ C. and $K = ·00406$ best satisfy observation.

TABLE I.

x.	a.	y.	
		Calculated.	Observed.
30°	9·75°	15·9	15·8
40	9·82	24·4	24·2
50	9·85	33·4	33·4
60	,,	42·9	43·1
70	,,	52·9	53·0
80	9·9	63·2	63·4
90	,,	74·2	74·1
100	,,	85·5	85·1
110	,,	97·4	97·7

TABLE II.

x.	a.	y.	
		Calculated.	Observed.
30°	9·6°	13·5	13·2
40	9·65	20·3	20·3
50	9·70	27·8	27·8
60	9·75	35·7	35·7
70	,,	43·8	44·0
80	,,	52·6	52·7
90	9·80	61·9	61·9
100	,,	71·7	71·4
110	9·85	81·8	82·4
120	,,	92·6	91·6

Table II. exhibits the agreement of the calculated and observed values of y when these constants are inserted in the equation to the curve. To calculate E.M.F. (E_B), the data are the same as were used in the calculation of E_A, except that the resistance in the primary circuit was 259·6 ohms.

$$\therefore E_B = ·00406 \times 1·03 \times 10^8 \times \frac{·00246}{259·6}(x-a)\left(140 + \frac{x+a}{2}\right)$$

$$= 3·96(x-a)\left(140 + \frac{x+a}{2}\right) \text{ C.G.S. units.}$$

Hence for the thermoelectric power (e_B) at the mean temperature t, we get

$$e_B = +555 + 3\cdot96t \text{ C.G.S. units.}$$

The mean of e_A and e_B being denoted by e_{pt-c}, we get

$$e_{pt-c} = +566 + 3\cdot94t \text{ C.G.S. units,}$$

the result quoted in equation (2) above.

Thermoelectric Power of Carbon.

In order to find the position of carbon on the thermoelectric diagram, I determined the line on this diagram of the platinum employed in the above experiments.

A strip of commercial lead, about 80 centims. long, had the platinum wires soldered to the ends. The general arrangement of the apparatus and the precautions used were similar to what have already been described above. Curve D shows the results of the observations ; the ordinates and abscissæ being the same as in the curves A, B, C. It will be noticed that the observations lie well on the mean curve, thus showing that the arrangements were not defective in any essential point.

Assuming $$y = K(x-a)\left(T - \frac{x+a}{2}\right)$$

as the equation to the curve, as above, I find that $T = -85°$ C. and $K = \cdot004815$ give results agreeing best with observation. (See Table III.)

TABLE III.

x.	a.	y. Calculated.	y. Observed.
30°	13·1°	8·67	9·05
50	,,	20·7	20·6
70	,,	34·6	34·7
90	,,	50·5	50·8
110	,,	68·3	68·2
130	,,	88·1	88·0

The data for calculation are :—

Resistance of primary circuit . . . . = 1001 ohms.
Mean observed E.M.F. of the Grove cell employed . . . . } = 1·75 volt.

Hence the E.M.F. of the lead-platinum couple and the thermoelectric power of platinum are, respectively,

$$E = \cdot004815 \times 1 \cdot 75 \times 10^{8} \frac{\cdot00246}{1001}(x-a)\left(85 + \frac{x+a}{2}\right);$$

$$\therefore E = 2 \cdot 07(x-a)\left(85 + \frac{x+a}{2}\right) \text{ C.G.S units,}$$

$$\therefore e_{pt} = +176 + 2 \cdot 07t \text{ C.G.S. units.}$$

The current would be from Pt to Pb across the hot junction.

Using this value for e_{pt}, we find for the thermoelectric power of carbon

$$e_c = -390 - 1 \cdot 87t \text{ C.G.S. units.}$$

This is the result quoted in equation (1) above.

In the table of thermoelectric powers given by Everett ('Units and Physical Constants,' § 186) there are given

$$\text{for Zn, } e_{zn} = -234 - 2 \cdot 40t,$$

$$\text{,, Ag, } e_{ag} = -214 - 1 \cdot 50t.$$

The value for e_c shows that the place of carbon in the table is between zinc and silver. In the thermoelectric diagram it is easy to see that for temperatures below 50° C., the line for carbon lies below that for cadmium, taking the value for e_{cd} from Everett's table (*loc. cit.*).

Concluding Remarks.

The disintegration preceding complete destruction of the carbon filament in an incandescent lamp, described by Mr. W. H. Preece, F.R.S., in a paper read before the Royal Society on March 26, 1885, is doubtless the result of molecular changes in the structure of the filament produced by the continued maintaining of the filament at an extremely high temperature. In my experiments, keeping carbon at a moderately high temperature altered the molecular condition of this material, the alteration being manifested as a change in the thermoelectric power of the carbon.

Physical Laboratory, University College,
        London, June 1885.

XV. *On the Use of Daniell's Cell as a Standard of Electro-
motive Force.* By J. A. FLEMING, *M.A., D.Sc. (Lond.),
Fellow of St. John's College, Cambridge, Professor of Elec-
trical Technology in University College, London* *.

[Plate V.]

THE extensive use now being made of strong currents of
electricity for purposes of illumination necessitates the
employment of instruments for measuring current-strength
and electromotive force of high values.   The employment of
electricity for telegraphic purposes, and especially in sub-
marine telegraphy, compelled attention to a common accuracy
in measurement of resistance and capacity; but for these
purposes the measurements of electromotive force and currents
are not of such importance as they are in the recent develop-
ments.   This requirement has drawn the attention of electro-
mechanicians to the subject, and led to the introduction of
numerous forms of electromotive force and current-indicators,
variously called potential galvanometers, voltmeters, pres-
sure-gauges, ampere- or am-meters.

Considering first the voltmeters, they may be classified,
according to Sir W. Thomson's nomenclature, into two classes
—idiostatic and heterostatic.   In the second class the magnetic
force at a point in the neighbourhood of a conductor con-
veying a current is compared with another magnetic field
either of the earth or of a permanent magnet, and the differ-
ence of potential at the ends of the conductor deduced there-
from.   In the first class no magnetic field is made use of other
than that created by the current itself.

In the case of heterostatic instruments the readings require
to be controlled by a special determination of the value of the
auxiliary field; and in the case of an ordinary tangent- or sine-
galvanometer, the determination of the earth's horizontal
magnetic force is a task requiring great care and considerable
precautions.   In the idiostatic instruments, in many cases,
springs are used to obtain a force with which to compare the
magnetic force in the neighbourhood of a conductor.   The
elasticity of these springs is not necessarily permanent, and is
liable to change by temperature as well as time.   Accordingly
in these instruments also, the constant must from time to
time be determined.   Pending the appearance of the new
instruments promised by Sir W. Thomson, in which no
springs nor permanent magnets are used, it is necessary to
fall back upon galvanic cells to establish a standard of elec-

---

* Communicated by the Physical Society: read June 27, 1885.

tromotive force, and the present paper is a brief collection of facts concerning the use of Daniell's cell for this purpose, and its application in the measurement of currents of various strengths. In all the experiments and methods cited below the cell has been used only to create a difference of potential, and not allowed to send any but a very small current, the means employed for comparisons being a slight modification of Clark's potentiometer, as shown in fig. 1 (Plate V.). On a stout mahogany board are fastened down two boxwood scales, each 5 feet long, divided into inches and tenths; these scales are fixed about $\frac{1}{4}$ inch apart and parallel, so as to form a groove between them. On these scales are stretched two fine uniform German-silver wires A B, A′ B′, about ·013 inch in diameter, and having a resistance of about 1 ohm to the foot-run: one end of both wires is soldered to a thick copper junction-piece J, and the other ends respectively to copper pieces connected to terminals M, M′. The wire thus forms one length of about 10 feet stretched over two scales. This forms the potentiometer wire ; its length is divided by the scale into 1200 parts, and each tenth of an inch can be divided by the eye into 10, making a possible division of 12,000. To the terminals M, M′ are connected five or six large-gravity Daniell cells, and the poles of this battery are short-circuited by an Edison 16-candle lamp of 240 ohms cold resistance. This enables the battery to keep a more constant difference of potential between the terminals M, M′.

A very constant E.M.F. can be obtained by using small accumulator-cells in series : the poles being joined by a carbon-filament lamp, and the leads to the terminals M, M′ taken off from the opposite sides of the lamp.

It is easy to calculate what number of cells are required to maintain a given difference of potential, say 2 volts, at the extremities of the potentiometer-wire. For let n be the number of cells, e the E.M.F. of each, and r the internal resistance, and let R be the resistance of the lamp and potentiometer-wire combined, and v the required difference of potential desired at the terminals M, M′; then

$$v = \frac{ne\mathrm{R}}{nr + \mathrm{R}},$$

which determines n. If r is not known, it can be determined by a second experiment, in which v is observed in the case of a given number of cells.

The current along this German-silver wire makes a fall in potential at about the rate of 1 volt in 5 feet. On one side of

the board is fastened a broad copper strap bb, having six terminals fastened upon it.   Between the last of these terminals and the end of the scale-wire A′ is inserted a reflecting-galvanometer of 5000 ohms resistance, and an additional resistance of 50,000 ohms R.

To the other terminals s, s on this copper strip are connected one pole (like to the pole of the battery B connected to M′) of each of the cells c, c' to be compared ; and the other poles of these cells are connected with sliders S, S′ travelling over the wires.   These sliders are blocks of wood sliding in the groove between the scales, and overhanging the wires.   On them are German-silver spring-strips as shown in the figure, and which, when pressed down, make contact with the wire.   The strips are backed with leather to avoid the production of thermoelectric currents.   By using two or more of these sliders, it is easily seen that several cells may be balanced at once on the potentiometer; and in particular two cells c and c' can be compared in respect of electromotive force very accurately, even although the E.M.F. of the main battery is not quite constant.   The introduction of the resistance R prevents any but the very smallest currents passing in the cells when the place of balance is being found on the potentiometer.   The German-silver strips g, g on the sliders make contact only when pressed down; so that in the normal condition the cells c, c' are insulated.   With the galvanometer in a sensitive condition it is very easy to read a difference of $\frac{1}{10000}$ of a volt on the wire, and $\frac{1}{1000}$ can be read with great accuracy.

Electromotive forces are read off directly as lengths, since the E.M.F. of the cells c, c' is directly as the distance of the constant points of their respective sliders from the end A′ of the wire.   Great care has to be taken in the first instance to stretch the wire uniformly, and to calibrate it if it presents any want of uniformity of resistance.   Provided with this convenient means of directly comparing electromotive forces, attention was next directed to a modification of Daniell's cell suitable for the experiments required.   In Dr. Alder Wright's extensive researches on the subject[*], the form of cell employed was that sometimes called Raoult's form, in which two small beakers contain the two solutions, and are connected by an inverted Y-tube, the ends of which are tied over with thin

* "On the Determination of Chemical Affinity in Terms of Electromotive Force.—Part V. On the Relationships between the Electromotive Force of a Daniell Cell and the Chemical Affinities involved in its Action."   Proceedings of the Physical Society of London, Vol. V. Part I. p. 44 *et seq.* [Phil. Mag. vol. xiii. p. 265.]

bladder. This form of cell is undoubtedly convenient for some purposes, but not for others, as when the cell has to be heated or cooled for comparison at different temperatures. Moreover, the siphon becomes filled in a very short time with a mixture of solutions by diffusion; and if the levels of the liquids are not exactly equal, a siphoning action is added to that of diffusion in carrying liquid over from one side to the other. After some numerous trials of all existing forms which have been proposed for Daniell's cell, the following was devised, which, though more bulky than others, has yet given great satisfaction, and has the great recommendation of always standing ready for use.

A large U-tube, about $\frac{3}{4}$ inch diameter and 8 inches long in the limb, has four side tubes (see Pl. V. fig. 2). The two top ones, A and B, lead to two reservoirs Z and C, and the bottom ones C and D are drainage-tubes. These side tubes are closed by glass taps. The whole is mounted on a vertical board, with a pair of test-tubes between the limbs. Suppose, now, a Daniell's cell is to be formed with solutions of zinc sulphate and copper sulphate, and that the zinc-sulphate solution is the denser. The left-hand reservoir S Z is filled with the zinc solution, and the right-hand reservoir S C with the copper solution. The electrodes are zinc and copper rods, Zn and Cu, passed through vulcanized-rubber corks, P and Q, fitting air-tight into the ends of the U-tube.

The operation of filling is as follows:—Open the tap A and fill the whole U-tube with the denser zinc-sulphate solution; then insert the zinc rod and fit it tightly by the rubber cork P. Now, on opening the tap C the level of the liquid will begin to fall in the right-hand limb but be retained in the closed one. As the level commences to sink in the right-hand limb, by opening the tap B copper-sulphate solution can be allowed to flow in gently to replace it; and this operation can be so conducted that the level of demarcation of the two liquids remains quite sharp, and gradually sinks to the level of the tap C. When this is the case, all taps are closed and the copper rod inserted in the right-hand limb.

Now it is impossible to stop diffusion from gradually mixing the liquids at the surface of contact; but whenever the surface of contact ceases to be sharply defined, the mixed liquid at the level of the tap C can be drawn off, and fresh solutions supplied from the reservoirs above.

In this way it is possible to maintain the solution pure and unmixed round the two electrodes with very little trouble; and the electrodes, when not in use, can be kept in the idle cells or test-tubes L and M, each in its own solution. In making

experiments concerning temperature, the whole U-tube can be immersed in a vessel of water or ice up to nearly the top of the reservoirs, and the temperature in the solutions taken by means of a thermometer passing through the rubber-cork. Each of the electrodes can be removed for examination or change without in the least disturbing the surface of contact of the solutions. If experiments are being made in which the sulphate-of-copper solution is the denser, the position of the solutions is interchanged. The bottle R serves to collect the waste solutions.

The electrodes are made of rods of the purest zinc and copper, about 4 inches long and $\frac{1}{4}$ inch diameter. The zinc found most suitable is made from zinc twice distilled and cast into rods ; the copper prepared by electro-depositing on a very fine copper wire, until a cylinder of the required thickness is obtained.

With these appliances to hand, all the facts recorded by previous experimenters have been carefully repeated and confirmed, and the influence of each variable upon the electromotive force examined. The results are collected as follows. For the sake of brevity, a Daniell's cell in which zinc, sulphate of zinc, sulphate of copper, and copper are the elements will be called a normal Daniell; and the statements here below refer to the variations in the difference of potential between the poles of the normal Daniell, when sending either no current or only an infinitesimal one, caused by variations in the physical state of the four elements. In each set of experiments the greatest care was taken to keep all the elements constant, except the one which was purposely being varied in order to detect the influence of it on the whole electromotive force.

1. *The Effect of Variation in the Copper Surface and Condition.*

In these experiments the copper- and zinc-sulphate solutions were sometimes of the same specific gravity, sometimes different; and in some cases the zinc electrode was a rod of the purest cast zinc amalgamated with pure mercury, sometimes a rod of commercial zinc wire cleaned but not amalgamated. Some scores of observations were made with identical zinc plate and solutions, but various kinds of copper plates[*];

---

[*] All the following values are given in real volts, taking Lord Rayleigh's value for the mean B.A. unit of resistance as equal to ·9867 earth-quadrant per second.

The determinations have been made against a Clark cell, kindly compared by Lord Rayleigh with his No. 1 cell, whose value is given in his

and all observations have confirmed the conclusions of Dr. Alder Wright that the most uniform results are obtained from copper plates freshly electrotyped over with a new clean pinkish surface of virgin copper, when the plate is taken straight out of the electrotyping bath and put into the cell without any delay or touching except a slight rinse with distilled water. The result of comparing a freshly electrotyped rod with a rod scraped and glass-papered, was to show that the scraped copper rod gave a higher electromotive force by about 4 parts in 629, or 6 parts in 1000. When both rods were freshly electrotyped in the same bath, and inserted in the same cell, there was absolutely no difference between them. Cells were compared with solutions of equal density 1·2 at 15° C. and amalgamated pure cast zinc, but different copper rods, as follows :—

	E.M.F.
Electrotyped copper rod . .	1·105 volt.
Scraped copper rod . . .	1·111 „

The exact amount of difference varied slightly in other experiments ; but with equally clean surfaces, the electrotyped fresh surface has a lower electromotive force than the scraped. The effect of amalgamating the copper rod is, like electrotyping, to lower its value below that of the clean scraped, but it is not so uniform. The following are values obtained from equal copper rods in the same cell, one having an electroplated surface and the other being slightly amalgamated with pure mercury :—

Freshly electro-deposited copper rod.	Freshly amalgamated copper rod.
1·103	1·104
1·106	1·104
1·105	1·104
1·106	1·105

The mean of the values of the electro-deposited copper exceeds by about 1 in 1000 the mean of the amalgamated copper ; but if the amalgamation is done thickly it causes

---

paper in the Phil. Trans. part ii. (1884) as 1·435 true volt at 15° C. My standard, called hereafter F_{20}, is greater than this by 3 parts in 4940, or is 1·436 volt at 15° C.; and experiments have shown that its variation-coefficient is nearly that found by Lord Rayleigh, viz. ·082 per cent. per degree diminution of E.M.F.

Accordingly, the value of this standard Clark cell F_{20} has been taken as equal to

$$1·436(1 - ·00082\ t°)\ \text{volt at}\ t°\ \text{C.,}$$

and all values given in the text are in terms of this.

more serious deviations, and though more convenient is not quite so reliable as electroplating the rod with fresh copper, but is preferable to employing simply a scraped or glass-papered surface of rolled copper. A large series of determinations were next made on the effect of oxidation of the copper surface. If a copper rod, newly electroplated, is left in the copper-sulphate solution, it gradually gets oxidized and covered with brown patches of oxide, and if amalgamated, the mercury sinks in and the surface gets brown and patchy. When this is the case the electromotive force rises, and by uncertain amounts, depending on the degree of oxidation. It is very remarkable how small a trace of brownish oxidation on the surface raises the electromotive force several parts in 1000, amounting in some cases to nearly 1 per cent. The following is one set out of many experiments on this point:—

Two solutions of zinc and copper sulphate were prepared of the pure crystals. The specific gravity of the zinc sulphate was 1·4, and that of the copper sulphate was 1·1. A rod of pure unamalgamated zinc and one of electrotyped copper was also taken. Keeping all other conditions constant, the rod of copper was first cleanly and carefully electrotyped over with a new fresh surface of copper, and exhibited no trace of oxidation; and the E.M.F. of this cell was then taken against a carefully tested standard Clark cell of known value ; and the rod was then suffered to oxidize on the surface by successive exposure to the air, the E.M.F. of the cell being taken at each stage.

		E.M.F. of cell.
Copper,	perfectly pure, unoxidized . .	1·072 volt.
,,	slightly oxidized, brown spots.	1·076 ,,
,,	more oxidized	1·082 ,,
,,	covered with dark-brown oxide film	1·089 ,,
,,	cleaned, replated with fresh pinkish electro-surface . .	1·072 ,,

Many other experiments of this sort showed the same thing. A Raoult cell was formed by taking two beakers, one containing zinc sulphate of specific gravity 1·2, and the other copper sulphate of the same specific gravity, and using amalgamated cast zinc and electro-deposited copper rods. The beakers were connected, when required, by a piece of clean cotton-wick dipped in water, and connecting both solutions by dipping into each. The copper pole was first freshly electroplated, and the following values obtained for the E.M.F. of the cell as it gradually oxidized :—

	E.M.F. of cell.
Freshly electro-deposited surface of copper	1·105 volt.
Slightly oxidized, faint brown tinge . . .	1·106 ,,
More oxidized	1·107 ,,
Still more oxidized	1·109 ,,
Re-electroplated surface	1·105 ,,

Hence these and many similar experiments all teach that oxidization, even the slightest trace, of the copper raises the E.M.F.; and that, in order to get the real value proper to the combination, the copper must be electrotyped over with a thin pure film of copper, and exhibit no trace of brown spots of oxide, and be used at once.

2. *The Effect of Variation in the Zinc Surface and Condition.*

Numerous experiments have been made to investigate whether there is any certain difference between zinc amalgamated or unamalgamated or cast or rolled. There is very little, if any, certain difference between perfectly pure cast zinc unamalgamated and the same amalgamated with pure mercury. There are greater differences if the zinc is not pure, and variations are introduced if impure mercury is used for amalgamation, all of them uncertain in amount.

The effect of oxidation of the zinc is to lower the electromotive force. If the bright surface of the zinc becomes tarnished, it always shows a slightly lower E.M.F. The smallest deposit of copper upon the zinc, due to diffusion of the copper salt into the zinc, is indicated by a marked depression, amounting to 2 or 3 per cent. On the whole, the only consistent values are obtained from chemically pure zinc with a bright fresh untarnished surface, whether amalgamated or not ; and the best results are given with pure zinc amalgamated with pure mercury. In Dr. Alder Wright's memoir the above conclusions are enforced by tabulated results of most extensive experiments.

On the question of amalgamation of the zinc we may quote a note on the subject by M. G. Lippmann in the *Journal de Physique.* There is an opinion expressed by some authors that amalgamated zinc has a higher E.M.F. than unamalgamated, even if pure. If a plate of each of the two substances be immersed in sulphate-of-zinc solution, a couple is formed in which amalgamated zinc forms the negative pole, inasmuch as it is the more readily acted upon by oxygen. Such, at least, is the result obtained if ordinary commercial zinc is used and ordinary sulphate-of-zinc solution. In a recent work, M. W. Robb shows that if care be taken to use electro-deposited zinc,

and also zinc-sulphate solutions deprived of free acid, the element zinc, zinc sulphate, and amalgamated zinc will not manifest any appreciable E.M.F. The superiority of amalgamated zinc over ordinary zinc is easily explained ; but when pure zinc is used, deprived of any oxide on the surface by slight rinsing in dilute sulphuric acid before placing it in the sulphate of zinc, there is little or no certain difference, to the extent of 1 part in 1000 in the case of the normal Daniell, between the pure zinc amalgamated or unamalgamated.

3. *The Influence of Density of the Solutions on the Electromotive Force.*

The chief reason for the differences in the values assigned by various observers to the E.M.F. of the normal Daniell is due to the great influence that the specific gravity of the two exciting solutions exerts on the resultant E.M.F. of the combination ; and the general law of the effect is this—If a Daniell cell be formed of amalgamated pure zinc, freshly-electrotyped copper, and solutions of pure zinc sulphate and copper sulphate of equal specific gravity, then, taking this cell as a standard of reference, increasing the density of the zinc sulphate lowers the electromotive force, and increasing the density of the copper sulphate raises the electromotive force, within, at any rate, the limits of density from 1·01 as an inferior, up to saturation as a superior limit. Zinc sulphate saturated at 15° C. has a density of a little above 1·4, and copper sulphate similarly saturated 1·2 ; and Dr. Alder Wright shows by experiments that the increment and decrement of E.M.F. for identical increment or decrement of density of both solutions are so nearly equal that for equally dense solutions, within limits, the E.M.F. is independent of the absolute density of both. This fact has been confirmed by many other observers. Amongst other careful experiments may be noticed those of Carhart *, whose experiments were specially directed towards ascertaining the influence which variation in the density of the zinc sulphate exerts on the resultant E.M.F.

In using a Daniell cell as a laboratory standard it is necessary, therefore, to prepare and standardize the solutions of zinc and copper sulphates with the same care as if they were to be used for volumetric analysis. It is a good plan to prepare two large stock bottles of solutions, and having carefully determined the density to adjust them to known specific

---

* A paper read before the American Association for the Advancement of Science, Sept. 5, 1884. See 'Telegraphic Journal and Electrical Review,' vol. xv. p. 250.

gravity by the aid of the specific-gravity bottle or hydrometer. For general use two standard solutions of each salt are specially useful. First, a solution of sulphate of copper very nearly saturated at 15° C. and having a specific gravity of 1·200, and a solution of sulphate of zinc of equal density. Secondly, a solution of sulphate of copper of density 1·100 at 15°, and a solution of sulphate of zinc of 1·4. These last values are chosen because they were employed by Sir W. Thomson in his standard gravity-cell ; and they can be used in either his form of gravity-cell, or in the U-tube form above, or in Raoult's form of separate vessels and siphon *.

A very large number of comparisons have been made of the E.M.F. of cells set up with these solutions and the E.M.F. of Clark's cells, whose value has been compared directly with cells standardized in absolute measure.

If a Daniell cell is carefully made up, either in the Raoult form or U-tube form, of solutions of pure zinc and copper sulphate not sensibly interdiffused at the level of contact, and with pure amalgamated cast zinc and freshly electrotyped copper plate, which is evenly plated with a new uniform pinkish deposit of electro-copper free from all brown spots of oxide, the E.M.F. of this cell, taken at once, is very close to 1·102 true volt, and the ratio of the E.M.F. of this cell to a corrected Clark cell at 15° C. is very nearly ·768 to unity † ; the Clark cell being taken as 1·435 at 15° C.

If, instead of taking the equidense solutions, we take zinc sulphate of specific gravity 1·400 and copper sulphate of 1·100 at 15° C., and the same plates, the E.M.F. of the cell lies close to 1·072 volt, and the ratio of the E.M.F. to that of the corrected Clark is ·747.

If, however, instead of taking the electromotive force at once after the freshly electroplated copper pole is introduced into the cell, the cell is allowed to stand an hour or so, both the above values will be increased by about ·003 volt, pro-

---

* If 28·25 parts by weight of pure crystallized sulphate of copper ($CuSO_4, 5OH_2$) are dissolved in 71·75 parts by weight of distilled water, the resulting solution will have very nearly a specific gravity of 1·200 at 18° C. ; and if 16·5 parts of the crystals are dissolved in 83·5 parts of water, the solution will have a density of 1·100 at 15° C.

For the zinc-sulphate solutions take 55·5 parts by weight of crystallized zinc sulphate ($ZnSO_4, 7OH_2$) and dissolve in 44·5 parts of distilled water. The resulting solution will have at 20°·5 C. a specific gravity of 1·400.

If 32 parts by weight of the crystals are dissolved in 68 of water at the same temperature, the solution will have a density of 1·200. These are useful densities.

† Lord Rayleigh assigns a value very close to ·770 for this ratio, and Dr. Alder Wright ·765. The figure in the text is derived from about 50 experiments of my own.

vided always that no interdiffusion of solutions has taken place, and that the zinc retains a perfectly bright untarnished surface.

4. *Influence of Temperature on the Electromotive Force of the Normal Daniell Cell.*

The researches of experimenters who have studied the Clark cell have established the fact that its E.M.F. diminishes with rise of temperature. The exact value of the coefficient of variation seems to depend on the mode in which the cell is made up ; and very careful examination has been made of the Daniell cell as above described, to see if its real E.M.F. is affected by temperature. Some writers have asserted that it is ; but it is obvious that the variation of internal resistance must be eliminated entirely by the use of a null method of observation of the E.M.F. The condenser method is not a sufficiently accurate one to apply, and the potentiometer method is the most trustworthy.

Two U-tube cells were prepared with 1·4 sp. gr. zinc sulphate and 1·1 sp. gr. copper sulphate ; and these cells were respectively immersed, the one in a water-bath at 20° C. and the other in melting ice at 0°. A pair of zinc and copper poles was likewise prepared ; and when the solutions in the U-tubes had acquired the temperature of the baths, the E.M.F. of each cell was taken with the pair of zinc and copper plates, first in one and then in the other, with the following results :—

Plates in the warm cell at 20° C. E.M.F. of cell.	Plates in the cold cell at 0° C. E.M.F. of cell.
1·081	1·082
1·079	1·082
1·079	1·082
1·078	1·083

The experiments showed a very small but decided fall of E.M.F. as the cell is warmed, and at the rate of about 3 parts in 1000 for 20° C. This is only about $\frac{1}{50}$ of the variation of a Clark cell for the same range ; and, practically, we may say that the E.M.F. of a Daniell cell is independent of temperature for such range as occurs in the natural temperature of the air in our climate *. This quality of the normal Daniell

---

* The same result has been obtained by Mr. Preece in his experiments on the effects of temperature on the electromotive force and resistance of batteries, see 'Electrician,' March 3, 1883, vol. x. page 367. He gives a table showing the E.M.F. at various temperatures, obtained by the condenser method, and shows that there is no perceptible change in E.M.F. of a normal Daniell between 0° and 17°, and a slight fall subsequently of about 9 parts in 1000 between 17° and 28°, but a rise, however, after reaching 63°.

is very important, and goes very far towards helping it to sustain its position as a standard cell against its rival the Clark cell.

The various coefficients of temperature-change which have been found for Clark cells indicate that it is unsafe to rely upon any cell taken at random, whose history is unknown, having a coefficient of variation accurately the same as that of the cells whose coefficients have been actually determined.

It would be a great advantage if instrument-makers would construct these cells in the form suggested by Lord Rayleigh —enclosed in a test-tube and having gutta-percha-covered leading-in wires passing through a rubber stopper. The co-efficients of variation would then be easily obtained for any cell, just as those of standard resistance-coils are ascertained and marked on each cell with the range of temperature over which it is applicable.

As a check on the foregoing experiments on the Daniell, the coefficient of variation of the standard Clark cell used was obtained. Two cells were taken, exactly equal at 18° C., and one of them was immersed for 48 hours in melting ice. The difference on the potentiometer-wire was then obtained between this cold cell and its fellow kept in water at 18° C. The potentiometer-readings were as follows :—

	i.	ii.	iii.
B, cell at 0° C. . .	961	971	974·4
A, cell at 18° C. . .	947	957	960
	14	14	14·4

From the experiment 1 the reading for the warm cell would have been $947 + \frac{14}{6} = 949\frac{1}{3}$ at 15° C. And hence the coefficient of variation is $\frac{14}{18}$ in $949\frac{1}{3}$, or ·0819 per cent. in the neighbourhood of 15° C. Lord Rayleigh gives ·082 as the value for his cells. It is obvious that Clark's cells cannot be used for standardizing galvanometers without a careful determination of their coefficients of variation.

The normal Daniell cell has a certain advantage in that when null methods for determining electromotive force are employed, its value is independent of temperature throughout a consi-derable range.

By the employment of the above two instruments—a poten-tiometer as described and a standard normal Daniell carefully constructed with all the precautions named—it is very easy to make very accurate measurements of strengths of currents of large magnitude. If a resistance is formed of such character that the current to be measured can be passed through it

without much affecting its temperature, and the potential measured at the extremities of this resistance by means of a comparison on the potentiometer between it and that of the Daniell, this gives at once the current.

In order to construct a resistance whose value at the instant of passing the current can be accurately measured, the following device is adopted :—On a board are mounted a series of copper blocks a, a, b, b, like the connection-pieces on a resistance-box (see Pl. V. fig. 3). These can be connected by plugs p, p. At opposite sides and ends are main terminals as M′ ; and the blocks a, b are connected by brass or German-silver wires wound in a spiral; similar coils of equal resistance connect each pair of opposite blocks. The number of coils must be an odd number.

If the plugs 1, 11, 3, 9, 5, 7 are put in, it is obvious all the coils $R_1, R_2 \ldots R_7$ are a series, and their resistance can be measured: call it r. If, then, the other pegs are inserted, the coils are now in multiple arc or parallel, and if there are n coils the resistance is $\dfrac{r}{n^2}$. By this arrangement the resistance in parallel can be inferred from the resistance in series ; and although each coil has a very small resistance, yet by using a large number, not only is a very easily measurable resistance obtained when the coils are in series, but a resistance of large current-carrying capacity when they are put in parallel.

The mode of using it is as follows :—The pegs are all put in, and the current to be measured is sent through the coils in parallel. By means of the potentiometer and standard-cell, the difference of potential is found between the terminals M and M′ when the current is passing. The alternate pegs are then removed, the current stopped, and the resistance taken of the coils in series, and the time noted which has elapsed between the measurement of potential and of the resistance. A few observations are taken of the resistance at intervals of time, by which to construct a curve of cooling; and by projecting back the curve, it is easy to ascertain very nearly the resistance at the time when the potential was measured. If small currents only are employed, it is not necessary to change the resistance; the current can be sent through it in series, and its resistance also measured in series. The writer has had constructed a large resistance of this kind at the Victoria Electric Lighting Station, for the measurement of dynamo currents up to 500 amperes. In this case the resistance consists of 36 wires of brass, No. 14 B.W.G., arranged in parallel, and of equal resistance. One of the wires can be disconnected and arranged instantly on a bridge to measure its resistance ; and in this

way, after measuring the potential at the ends of the 36 wires in parallel, with the current passing through them, one wire is disconnected, and its resistance taken immediately; from which observations it is possible to approximate very accurately to the resistance of the whole wires in parallel. In order to afford data for constructing such resistances, experiments were made of passing various currents through coiled spirals of naked wires of different sizes and materials.

A large number of wires were prepared, of copper, brass, iron, German-silver, each 25 feet long, and of six sizes respectively, Nos. 10, 12, 14, 16, 18, 20, B.W.G., the diameters being given below. These wires were coiled into spirals round wooden rods about one inch diameter, and the turns of the wire well separated, so that each coil or spiral was about 18 inches long. Measured steady currents were sent through these for some hours, and so adjusted that after the temperature had become steady the wires were all at a temperature just about bearable by the hand, that is near 60° C. The currents respectively carried were as follows :—

Size of wire.	No. 10 B.W.G. ·134 inch diam.	12 ·109	14 ·083	16 ·065	18 ·049	20 ·035
Currents carried in Amperes.						
German Silver ...	18·75	13·5	8·25	6	4·12	3
Brass	30	18·75	15	9·75	7·5	5·25
Iron	18	11·25	10·5	8·25	5·25	3·75
Copper	49·5	38	26·25	20·25	15	9

These currents passed through the above-described naked spirals bring the respective wires to about a temperature of 60° C., when equilibrium is established; and for the purposes of measuring currents not more than one third of the above currents should be used with wires of the size appended. Thus for 300 amperes, about 50 No. 10 B.W.G. wires will carry it without much sensible elevation of temperature; and by arranging 50 wires so that their resistance can be quickly measured in series, a resistance can be made suitable for measuring the potential at the ends of a known resistance.

By the use of this method it is easy to standardize any current or potential-galvanometer at any part of the scale, and obtain the absolute or corrected value of the deflections ; and

these methods have been employed with success for some time in standardizing the working galvanometers used in the lamp factory of the Edison and Swan United Electric Light Company.

In conclusion may be given other results, collected from various authors, respecting the electromotive force of the Daniell-cell.

Wiedemann (*Galvanismus*, vol. i. cap. iv., *Bestimmung der Electromotorischen Kraft*, p. 341) gives a description of Raoult's cell (see Raoult, *Ann. de Chim. et Phys.* [4] t. ii. p. 345, 1864), and states that Raoult finds that copper-foil has higher electromotive force than electro-deposited copper by about $\frac{1}{200}$; and attributes it to the oxides of copper contained in it. He also confirms the invariability of E.M.F. with temperature at least between $10°$ and $50°$; and states that with pure amalgamated zinc and electro-deposited copper, solution of saturated sulphate of copper and solution of sulphate of zinc, containing 1 part of crystals to 1 part of water = 1·35 sp. gr. at $20°$, the electromotive force is 1·124 electromagnetic units. This, corrected by the Cambridge value of the B.A. unit, is 1·109 volt.

Sir W. Thomson (p. 245 of 'Papers on Electricity and Magnetism') finds the electrostatic measurements of a Daniell's cell to be ·00374. The nature of the solutions and electrodes are not given. Taking the value of v as 3×10^{10}, we have the E.M.F. as 1·12 B.A. volt, which, reduced to true volts, gives 1·105 volt.

Lord Rayleigh gives the ratio of a Daniell set up with amalgamated pure zinc, electro-deposited copper, and solutions of sulphate of zinc and copper, each of sp. gr. 1·1. Five observations of the ratio of this cell to that of a known Latimer-Clark cell at $16°$ C., taken as unity, gave ·7702, ·7710, ·7705, ·7698, ·7702, mean ·7703 ; and since the Clark is 1·435 volt, this gives the Daniell as 1·105 volt.

Latimer Clark (*Journ. Soc. Tel. Eng.*, January 1873) gives it as 1·11, which, reduced to true volts, is 1·095; and Dr. Alder Wright (*Proc. Phys. Soc. London*, vol. vi. p. 292) gives the value of a normal Daniell set up with solutions of the same molecular strength, preferably of strength m M SO_4 100 OH_2, where m is near 2—that is with copper sulphate nearly saturated, and zinc sulphate of equivalent molecular strength, and pure amalgamated zinc plates and electro-deposited copper— as 1·114 B.A. unit, or 1·099 true volt.

None of these are very far from the value assigned to the standard cell described above, viz. 1·102 volt, with equidense solutions and metals as described.

XVI. *On Molecular Shadows in Incandescence Lamps. By* J. A. FLEMING, *M.A., D.Sc. (Lond.), Fellow of St. John's College, Cambridge, Professor of Electrical Technology in University College, London* [*].

SINCE presenting a short note on the above subject in 1883 many further opportunities have occurred for observing the conditions under which molecular shadows are formed in incandescence carbon-filament lamps, and of correcting one or

LINE OF NO DEPOSIT

COPPER DEPOSIT

BREAK
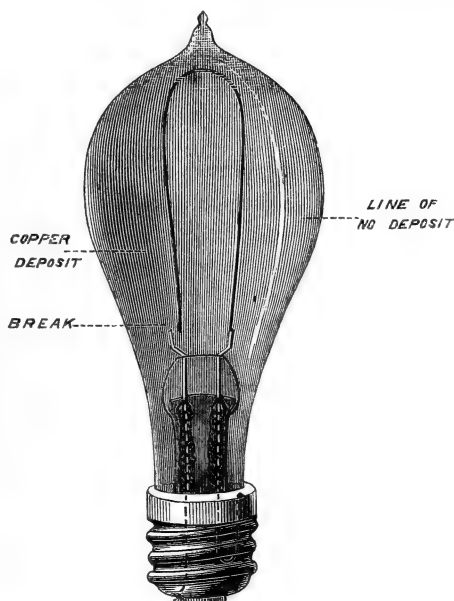
two statements then made. It has been observed in an immense number of cases, that not only do incandescence lamps become coated on the interior of the glass with a deposit of carbon, but that the envelope may have deposited upon it a metallic film, derived from the leading-in wires to which the carbon filament is clamped. In the Edison lamp the platinum wire only just passes through the glass, and is connected with copper wires broadened out into a clamp ; the filament is gripped in these clamps and then electro-plated over with copper to effect a good junction. In the Swan lamp the platinum wires are joined directly on to the carbon. It occasionally happens that there is an unusual amount of resistance at the clamps, or that by excessive electromotive force more current is forced through the lamp and more heat gene-

* Communicated by the Physical Society : read June 27, 1885.

rated everywhere.   In this case the tendency will always be
to increase and go on increasing the resistance, and, therefore,
the temperature at the point of highest resistance.   Suppose
this occurs on the clamp or on the leading-in wire, then ex-
perience shows that the metal is volatilized and deposited as a
film on the glass.   This metallic deposit is not uniform ; it is
thickest nearest the base of the lamp and gradually thins away
up to the crown, and at a certain height is thin enough to
transmit light.   It is not very uncommon to obtain Edison
lamps with this copper deposit.   The colour of transparent
copper is a fine sage green inclining to blue ; compared with
the colour of gold leaf seen by transmitted light, it very
closely resembles it.   On one occasion the writer obtained a
lamp with a silvery metallic film deposited over it on the
inside of the glass.   From the outside it had a mirror-like
lustre; on breaking the lamp this film was seen to be brownish
and not brushed off by the finger, but it could be removed by
scratching.   It was not removed by holding in the oxidizing
flame of a Bunsen burner : therefore it was not carbon.   It
was not removed by nitric acid; but on boiling a fragment of
the glass, covered with this metallic deposit, in nitro-hydro-
chloric acid the film disappeared.   It was therefore probably
platinum.   The film was transparent, permitting objects to be
seen through it, and transmitted brownish light.

Now, under certain circumstances, a line of no deposit is
formed on the surface in the plane of the filament, which is,
as it were, the shadow of one side of the loop   This indicates
that the process of molecular scattering, which is going on at
some spot on one or other clamp, is not a mere evaporation or
volatilization of the metal, but a projection of molecules in
straight lines in every direction.   The trajectory of the mole-
cules will be interfered with in some directions by the carbon
filament; and hence result lines and places of no deposit which
are molecular shadows of the loop.   On every other part of
the glass the molecules will inpinge and adhere, forming a
metallic coating.   From the facts that the free paths of the
molecules differ in length, and that the clamp is much nearer
to the neck of the lamp than to the crown, it follows that a
much larger proportion of the scattered molecules strike the
glass near the neck, and the thickness of the deposit is there-
fore a measure of the proportion of molecules which have a
free path, equal to the distance of that part of the envelope
from the scattering point.   Curiously enough the line of no
deposit, or shadow of the loop, is not always seen in copper-
deposited lamps.   This may be because the scattering is
going on from both clamps, and therefore the shadow on one

side is covered up by the shower from the clamp on that side. It has been noticed in one or two cases that small tufts of carbon are seen on one clamp, and that when a well-defined shadow exists on that side, this seems to indicate that the shower of copper molecules has been partly stopped by the opposite clamp, which has therefore acted like a target and become encrusted with a proportion of the molecules shot at it.

With respect, next, to carbon deposits. Every one knows the appearance of a lamp after it has been burning for some time or overburnt: it is clouded with smoke-like deposit. In nearly all cases of copper deposit the molecular shadow exists, but it is not nearly so often seen in the case of carbon deposits. After many observations it was found that the molecular shadow of the filament, or line of no deposit, could be formed by suddenly raising the filament to a very high temperature, as for instance by placing a 50-volt lamp for an instant on a 100-volt circuit; whereas when the deposit of carbon takes place slowly, and as it were in the natural way, the lamp exhibits only a general smokiness but no line. Again, it has been found that when a carbon filament is cut sharply through at one point, caused by excessive temperature at one spot, there is very frequently a sharply marked line of shadow of the loop on the side of the envelope farthest removed from the fracture. These facts seem to indicate that in normal use, when the lamp is not being pressed beyond the electromotive force at which it was intended to be used, there is a general evaporation of carbon going on from all parts of the loop, and these molecules, being projected with no abnormal velocity, probably collide with molecules of residual air a large number of times before they reach the walls of the envelope, and thus get their trajectories very much changed in direction. In this case the result would be to cause an irregular deposit of molecules of carbon on the glass envelope. But if we suppose a sudden or very excessive temperature to be given to part or the whole of the filament, this may cause a very violent projection of molecules of carbon from the filament; and these would pass outwards in straight lines, and a far larger proportion would reach the envelope in the direction in which they were first projected. This would then cause a deposit on all parts except those shielded by the loop; and in the case when such violent projection went on from all parts of the loop, as when a lamp is overheated, it is easily seen that parts of the envelope not lying exactly in the plane of the filament would receive twice as much deposit as those exactly in the plane. In most cases of carbon deposits the lamps

which give the best shadows are those made with single loop, but it has also been observed on Swan lamps with double twist. By making lamps with clamps of various metals, it might be possible to obtain metallic films of various kinds. Interesting magneto-optic phenomena might perhaps present themselves in the case of transparent iron films, if they could be obtained.

XVII. *Origin of Coral Reefs and Islands.*
By James D. Dana, *LL.D.**

[Plate I.]

THE Presidential Address of Dr. Archibald Geikie, Director-General of the Geological Survey of Great Britain, before the Royal Physical Society of Edinburgh in 1883 †, reviews the subject of the origin of coral-reefs and islands. In the course of the discussion, the author sustains and enforces the objections which have been presented by others, and concludes that " the existence of such reefs is no more necessarily dependent on subsidence than on elevation." The existing state of doubt on the question has led the writer to reconsider the earlier and later facts, and in the following pages he gives his results ‡. That both sides may be fairly before the reader, the views of Darwin and the evidences in favour of his theory are first considered, and afterwards the arguments that have been urged against it. Part of the objections are based on misunderstandings of the facts, and hence a general presentation of the subject has been thought necessary.

Part I.—*The Darwinian Theory and its Evidences.*

1. According to the Darwinian theory, islands with fringing reefs have been often changed through a slow subsidence of the region into islands with barrier reefs; and, as the last summit of the sinking land disappeared, the latter have become atolls, that is, barrier reefs enclosing simply a piece of the ocean (or a lagoon). Darwin added to this conclusion, a *second*, in view of the wide distribution of atolls and their

relations to other islands: that the subsidence indicated involved the whole central Pacific, besides other large areas. He also expressed the opinion that a Pacific continent had disappeared through the subsidence. The proofs of the first and the second conclusions are partly different and should not be confounded. The third is no necessary part of the general theory, was not adopted in my Report, and need not be further considered.

2. Darwin did not hold that atolls were necessarily evidence of a subsidence *now* in progress, but allowed that in some regions they may have reached a state of rest, and may perhaps have undergone an elevation since the cessation of the subsidence; and also that subsidence and elevation may have alternated.

3. Darwin found what he believed to be *almost certain proof of subsidence* in the features of the large barrier-islands and atolls. He perceived in the rocky islets that dot the great interior lagoon-like waters of the Gambier group, Hogoleu, and other similar barrier-islands of the Pacific, and the general resemblance of such islands to atolls, strong evidence, " leaving scarcely any doubt on the mind," that the islets were the emerged points of *sunken* lands ; that such barrier-islands were no less lagoon islands than Keeling atoll (the atoll which he investigated); and, if evidence of subsidence, the atoll was proof of further subsidence, that is, one that had continued to the disappearance of the sinking peaks.

The evidence which had satisfied him was satisfactory to me when I first learned of his views in Australia (in 1839), after a cruise amongst the Paumotu atolls and the Tahitian and Samoan reef-regions; and more decidedly so later, when I had been among the Friendly, Feejee, and other Pacific islands.

That the argument may be appreciated I here introduce a map of the eastern half of the Feejee Archipelago *. Several of the great barrier-reefs in this map, 10 to 20 miles in length, have but one or two peaks of the sunken land remaining; Nanuku has but one little point, near its southeastern angle, a mile of peak within a barrier island 200 square miles in area; Bacon's Isles are the last two little peaks of a still larger lagoon; and besides these and other examples of disappearing lands, a dozen of the easternmost islands are actual atolls—the last peak gone.

4. To this, the chief of Darwin's arguments in his own view,

---

* Reduced from the general map of the archipelago in the Atlas of the Wilkes Expedition.
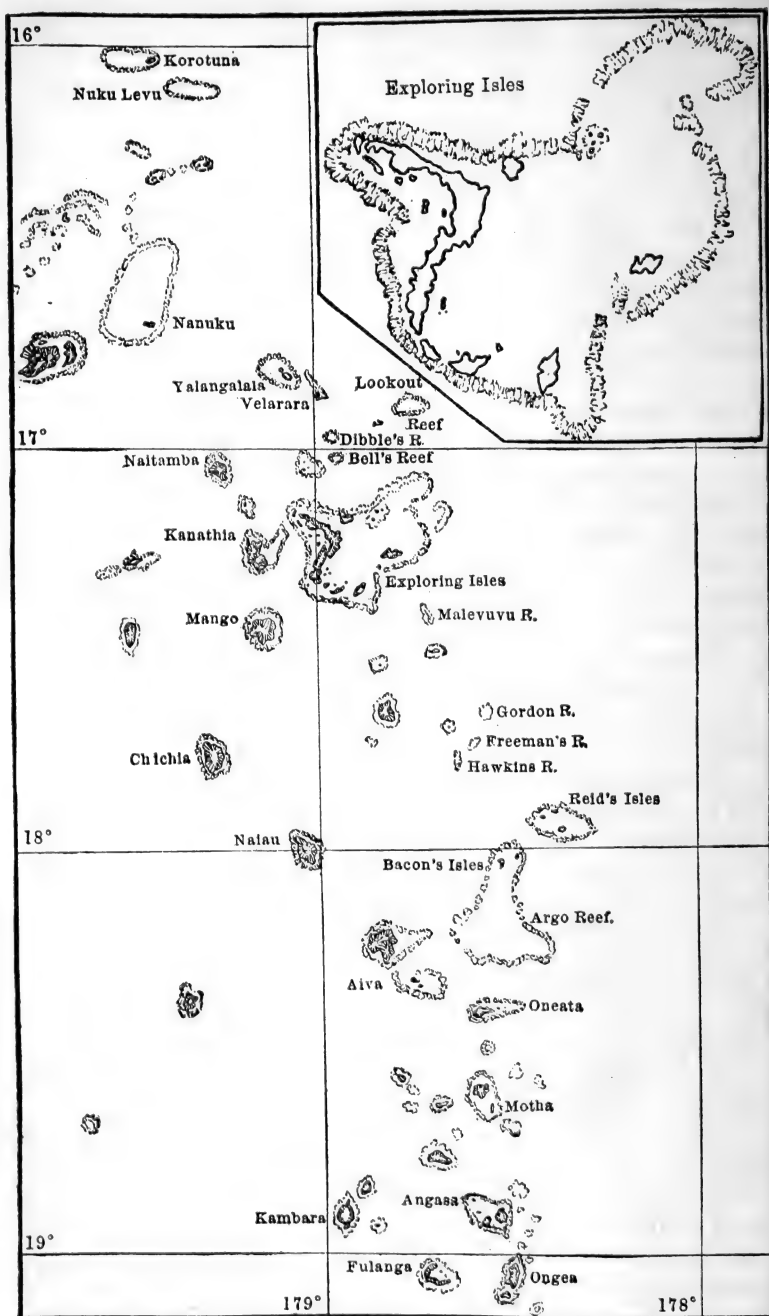
EASTERN PART OF THE FEEJEE ARCHIPELAGO.

another of like importance is added in my Report—*the exist-ence of deep fiord-like indentations in the rocky coasts of islands, both of those inside of barriers and those not bordered by reefs.*

When making the ascent of Mount Aorai, one of the two high summits of Tahiti (September 1839), where high narrow ridges, almost like a knife-edge along their tops, alterna-ting with gorge-like valleys 1000 to 3000 feet deep, radiate from the central peaks but die out in a broad even plain at the shores, I was made to appreciate the consequence to such an eroded land of a partial submergence. At any level above 500 feet, its erosion-made valleys would produce deep bays, and above 1000 feet fiord-like bays, with the ridges spreading out in the water like spider's legs. Observing on the maps of the Marquesas Islands precisely this condition, it was a natural inference that the lands had undergone great subsi-dence, and perhaps were still subsiding.

With this criterion of subsidence in view, the evidence from the Gambier and Hogoleu Islands is doubled in force ; and that for the sinking of Raiatea of the Tahiti group, re-presented in fig. 3 of the plate of maps in Darwin's ' Coral-Reefs,' is as strong from each of the two enclosed islands as it is from the great breadth of the reef-grounds; and the same is true for Bolabola, another Tahitian island on the plate.

So it is also in the Feejees. The demonstration as to sub-sidence in the large barrier-island called the Exploring Isles, for example, is made complete by the form of the ridge of land along one side of the great barrier, and the positions of adjoining islets.

5. The general parallelism between the trends of coral-islands and the courses of the groups of which they are part, and the courses also of the groups of high islands not far distant, were regarded by Darwin as confirming his view that the coral-islands were once high islands with bordering reefs.

6. Darwin uses also the argument that the large coral-islands have the diversity of form found in the barrier-reefs of high islands; and also that they often have such groupings as would come from the sinking of a large island of ridges and peaks with encircling reefs. He describes the Maldives as one example of the latter, and the two loops of Menchikoff island in the Caroline Archipelago as another.

7. The depth of lagoons, and of the channels inside of large barrier-reefs, afforded him further evidence of subsidence, it being in many cases two to three times greater than the limiting depth (120 feet) of living reef-making corals.

8. The great depth of the ocean in near vicinity to the atolls is another source of evidence added.

9. He urged also, in supporting his views, the non-existence in the ocean now, and the extreme improbability of existence at any time, of submarine volcanoes or chains of mountains having their numerous summits within a hundred feet of the surface.

10. Darwin speaks of smallness of size in coral-islands as a result of continued subsidence. In my Report I base an argument for subsidence on smallness in the proportion of dry land, and on smallness of size, when there is *gradation* toward either condition, and the seas beyond are free of islands. The facts bear on the general conclusion with regard to a Central-Pacific area of subsidence as well as on the fundamental point in the theory.

If an atoll-reef is not undergoing subsidence, the coral and shell material produced that is not lost by currents serves, (1) to widen the reef; (2) to steepen, as a consequence of the widening, the upper part of the submarine slopes; (3) to accumulate, on the reef, material for beaches and dry land; and (4) to fill the lagoon.

But if, while subsidence is in progress, the contributions from corals and shells exceed not greatly or feebly the loss by subsidence and current-waste, the atoll-reef, unable to supply sufficient débris to raise the reef above tide-level by making beaches and dry-land accumulations, would—(1) remain mostly a bare tide-washed reef; (2) lose in diameter or size, because the débris that is not used to keep the reef at tide-level is carried over the narrow reef to the lagoon by the waves whose throw on all sides is shoreward; (3) lose in irregularity of outline, and thus approximate toward an annular form; (4) lose the channels through the reef into the lagoon by the growth of corals and by consolidating débris; and (5) become at last a small bank of reef-rock with a half-obliterated lagoon-basin.

The Pacific contains reefs of the three kinds:—(1) atolls with much of the reef under trees and shrubbery; (2) others, of large and small size, with the reefs mostly or wholly tide-washed; (3) others only two or three square miles in area, without lagoons. Further, the kinds are generally grouped separately and gradationally. (1) The islands of the Paumotu and Gilbert Archipelagos have usually half or more of the reef dry and green; (2) the northern Carolines and the northern Marshall Islands, and the eastern Feejees, although in part of large size, are mostly bare reefs; while (3) the islands of the Phœnix Group, of the Equatorial Pacific east

of the line of 180°, are, with one exception (Canton or Mary), not over four miles long. The three more southern of the Phœnix Islands (see Map, Plate I.), Gardner's, Hull's, and Sydney, between 4° 25′ S. and 4° 35′ S., are two to four miles long, and have lagoons; five, including Phœnix, Birnie's, and Kean's, between 3° 10′ S. and 3° 30′ S., and Howland and Baker's, north of the equator, are a mile and a half and less in length, and have depressions at centre, but no lagoons. The depressions contain guano, and one of them, Kean's, has much gypsum mixed with the guano *; Kean's and Phœnix have a foot or two of water at high tide, the tide rising 6 feet. Another of the number, Enderbury's, is three miles long and has a half-dried lagoon, which is very shallow and has no growing corals †. To the north of these islands for fifteen degrees of latitude the sea is an open one ; and in the next ten degrees, to the line of the Hawaian Chain, the only islets not marked doubtful are " Coral-Reef, A wash " and Johnston Island.

A similar gradation in size takes place in the Ellice, Ratack, and many other groups of the ocean. Smallness of size, and dried lagoon-basins, with occasionally a deposit of gypsum from evaporated sea-water, are just the result that should have come, by the Darwinian theory, from subsidence; and gradation in size from gradation in the amount of subsi- dence. The positions of the Union, Gilbert, Ratack, and Ralick groups with reference to the Phœnix group are shown on the Map, Plate I. All of the islands on the map are coral- islands, and nearly all atolls; and the part of the encircling reef marked by fine dots is under water at high tide.

Adopting this view of the origin of these smallest of coral- made islands, I readily accepted Darwin's second conclusion as to a great central oceanic area of subsidence. The further inference, also, was deduced, for reasons stated in my Report, that the greatest amount of subsidence took place along a belt stretching south-eastward from the southern half of

---

* J. D. Hague, Amer. Journ. Sci. (II.) xxxiv. p. 242. Mr. Hague, in his valuable paper on the Guano Islands of the Central Pacific, mentions the existence of a bed of gypsum two feet thick under the guano of Jarvis Island, another small equatorial island, eleven degrees east of the Phœnix group.

† Baker's Island has a height of 22 feet, according to Mr. Hague, showing, he says, some evidence of elevation; and Enderbury's I found to be 18 feet in height, from which I inferred some elevation. But Howland's, Birnie's, McKean's, Phœnix, Gardner's, Hull's, and Sydney are not higher than ordinary atolls would be in a sea of 6-foot tide.

The facts with regard to the " Reef " on the map, in long. 175° W. and lat. 2° 40′ S., I have been unable to learn.

Japan and passing south of the Marquesas group toward
Easter Island, and a line was drawn on a map among its
illustrations representing the course of " the axial line of
greatest depression " *.

These deductions have been apparently sustained by the
soundings of the ' Tuscarora ' and ' Challenger ' in 1874,
1875, and 1876. The soundings of the ' Tuscarora ' through
the Phœnix group in 1875, on its route from the Sandwich
Islands to the Feejees (under the command of J. N. Miller,
U. S. N., by the order of the U. S. Hydrographic Bureau),
are shown on the map of the central Pacific herewith pub-
lished (Plate I.).

The soundings about these islands prove (1) that the
islands are situated within the deep 3000–4000-fathom area
of the ocean; and appear to indicate also (2) that along lines
transverse to the trend of the islands (or to the direction of
trend in other groups to the west), mean submarine slopes
of 1 : 1·5 to 1 : 7 exist; while in the direction of the trend,
the slopes are much less. The slope of 1 : 1·5, or that of the
angle 33° 41', is nearly the maximum slope of the sides of
Cotopaxi, Mt. Shasta, and several other volcanic summits of
Western America.

The facts are these:—

Halfway between Sydney and Birnie's Islands, 60 English
miles apart, a depth of 3000 fathoms (18,000 feet) was
found. Off Enderbury's Island (40 miles north-east of
Birnie's), (1) a depth of 2835 fathoms was obtained 20 miles to
the south-west; (2) of 880 fathoms 2½ miles to the south-west;
(3) of 1991 fathoms 3 miles to the north-east; and (4) of
2370 fathoms, 11 miles to the north-east. The mean slopes
to the south-west, calculated from the soundings 1 and 2, are
1 : 6 and 1 : 3; and to the north-east, from 3 and 4, 1 : 1·5 and
1 : 4 ; 14 miles south-*east* of Hull's Island, at right angles
to the above direction, a depth of 935 fathoms was found,
which gives the slope 1: 13.

Further evidence as to the submarine slopes about equa-
torial coral-reef islands is afforded by soundings, made under
the direction of the British Admiralty, near the very small
Swain's Island, at the south end of the Union group (see
map) : and others, by the 'Tuscarora' under Commander
Miller, in 1876, near the Danger Islands, about five degrees
east of Swain's. Off Swain's Island, two soundings, one

* Report, pp. 399 and 432, and map between pages 8 and 9.
  This line is reproduced on a chart of the World, in my ' Manual of
Geology,' where it is lettered A' A'.

south of it and the other east (the two directions at right angles to one another and the latter not diverging far from the trend of the other islands of the Union group), give the slopes 1:7 and 1:13. Off Danger Island, as Commander Miller's Report states *, the depth of 660 fathoms was obtained half a mile (nautical) off the south-west corner of the reef near south-east island, and 985 fathoms one mile east of the reef—corresponding to slopes 1:1 and 1:0·75. 1:1 is a steeper slope than occurs even in small dry-made cinder-cones ; and 1:0·75 (53° 8′) is steeper still.

The above facts are sufficient to authorize the drawing of the bathymetric lines for 1000, 2000, and 3000 fathoms *quite closely* about the islands of the Phœnix group, and to give the areas a northwest-southeast elongation, corresponding with that of the neighbouring Pacific islands to the west, as on the accompanying map, Plate I.†

It follows from the above-mentioned facts that the deep-water areas adjoining the Phœnix group, named provisionally by Petermann ‡ the " Hilgard depths " and the " Miller depths," are parts of one large area 1200 miles broad. The

* I am indebted for the soundings about Danger Islands to Commander J. R. Bartlett, Superintendent of the U. S. Hydrographical Bureau.

† The line on the map for 1000 fathoms is a simple dotted line ; that for 2000 fathoms, - - - - ; for 3000 fathoms, - - - -.

‡ *Geogr. Mittheil.* 1877, page 125 and plate 7. The deep areas along the lines of soundings were named by Petermann on his very valuable bathymetric map of the Pacific simply to facilitate reference.

The bathymetric lines about the islands on the accompanying Map (Plate I.) have an unreasonable degree of regularity. But with no facts to indicate the actual irregularities, none could be reasonably introduced. The trends given them are the same as on Petermann's map. The actual steepness of slope is probably not exaggerated for either of the islands. If similar slopes exist about the smaller islands in other parts of the ocean, the final bathymetric map of the Pacific will have a very different aspect from that presented by the maps hitherto published, and the Central Pacific a much greater mean depth. About Wakes Island, a small atoll in latitude 19° 11′, standing alone in the ocean six degrees north of the Ralick Chain, the width of the area enclosed by the 2000-fathom line, as drawn on Petermann's bathymetric map, is nearly 100 nautical miles, while, in view of facts at the Phœnix group, the actual width is probably not over 10 or 15 miles.

With but four lines of soundings for the part of the great Pacific Ocean, within 35 degrees of the equator, the author of a bathymetric map has to rely chiefly on his judgment or conjecture for the larger part of the surface. There are many great problems in physical, geological, and biological science that would be elucidated by the facts which a thorough bathymetric survey of the ocean would afford ; and the work is large and important enough to call for aid from each of the great nations of the world. Thus far, for the Pacific Ocean, the United States is first in the amount of work done.

greatest depth obtained in the part of the area south-west of
the group (400 miles broad) is 3305 fathoms, and in the part
north-east 3448 fathoms.

Again, the soundings of the 'Tuscarora' of 1875 here cited,
taken in connection with those of the same vessel in 1874,
under Commander George F. Belknap, along a line from the
Sandwich Islands westward to Japan (mostly between the
parallels of 20° and 25°), suggest the further conclusion, that
the deep-sea area of the central equatorial Pacific, in which
the Phœnix Islands stand, extends north-westward toward
Japan, and that it was crossed by the 'Tuscarora' between
171° E. and 150° E., where were found depths from 3009
to 3273 fathoms (with some alternations of smaller depths
that isolated areas may account for).   It is also probable
that the soundings of the 'Challenger' east of Japan be-
tween 153° E. and 143° E., and just north-west of those
of the 'Tuscarora,' were within the same deep-sea area.   If
this be so, a long deep-water area or trough extends from
Japan south-eastward through the Central Pacific, conform-
ing well to the suggestion of the Darwinian theory; and
corresponding in direction approximately to the " axial line
of greatest depression " referred to above—the line AA on
the accompanying map.

As regards the rest of the Central Pacific between the
above defined 3000–4000-fathom belt and the Hawaian chain,
the depths sounded by the 'Tuscarora' are, with few exceptions,
over 2400 fathoms; two thirds of them are over 2750 fathoms;
and a fifth (out of the fifty-five in this area) over 3000 *.

* The same two lines of soundings by the 'Tuscarora' suggest the
existence of a second long deep-sea belt or trough in the Central Pacific
just south of the Hawaian chain.   This supposed trough was crossed by
this vessel in 1875 between the parallels of 13° N. and 18° N. (" Belknap
depths "), and in 1874 between the meridians of 172½° W. and 177½° W.
(the " Ammen depths "); the greatest depth found on the former line is
3125 fathoms, and on the latter 3106 fathoms.   Should the existence of
these two troughs be sustained, the region between them would be a
Central-Pacific plateau ; having in it, along the 1875 line of soundings,
depths of 2972 to 1325 fathoms, and along that of 1874, depths of 2836 to
1108 fathoms ; the shallower portion is near the middle of each line of
soundings, has a great descent (6000 to 9000 feet) on either side, sug-
gesting the idea of a central ridge.   Over this plateau-area there are,
south of the Hawaian chain, two or three small coral-islands ; and
further eastward, the Palmyra, Kingman, Washington, Fanning, and
Christmas reefs and islands, which, although coral structures, make the
idea of a central ridge in this part for 600 miles almost a manifest fact.
Further east, the Marquesas Islands are in the same range.   The deep belt
lying on the south side of the plateau diminishes in depth to the east-
ward, the 'Challenger' soundings from the Sandwich Islands to Tahiti
finding no depth in the course of this belt greater than 2750 fathoms ; but

shores there are deep indentations and fiord-like bays, separated in some cases by narrow ridges, sometimes in spider-leg style; so that the proof of subsidence is positive, as explained in § 4.

Tahiti presents none of the Marquesan evidence of subsidence. Its erosion-made valleys, as already explained, die out at the broad shore-plain, and the island is comparatively even in outline. I found over it, like Darwin before me, no evidence of elevation beyond one or two feet at the most. It has broad reefs; and the channel inside the barriers between Papieti and Toanoa (2 miles) has a depth of 3 to 25 fathoms. From the width of the reef, and the slope (6 to 8 degrees) of the land, and of the lava-streams outcropping in the sides of the valleys, supposing this slope to be continued under water, I made the probable subsidence 250 or 300 feet. A slope of 6 degrees, and a width of reef of half a mile, gives 240 feet for the depth of the reef at the outer edge.

The Samoan (or Navigator group) includes (beginning at the east) Rose Island (an atoll), Manua, Tutuila, Upolu, and Savaii.

Manua has bold shores, a height of 2500 feet, and a narrow reef where any *. Tutuila is of the Marquesan type in its bold indented sides, and this suggests a probable subsidence. Pangopango Bay, in which we anchored in 174 feet of water, has a length of three miles. The coral-reefs are of the *fringing* kind where any occur. Upolu, a few miles west, has bold shores and small or no reefs for fifteen miles of its north shore, east of its middle ; but elsewhere there are broad reefs (mostly 5000 to 8000 feet in width) and a very gentle slope (three to six degrees) in the land above, which is about the slope of its underlying lava-streams. The great width of the reef seemed to be evidence of subsidence. But the absence on the north side of the island of a channel in the reef deep enough for any craft larger than canoes made it essentially a great fringing reef. A calculation from the width and land-slope gave about 260 feet for subsidence; but I add (on page 332 of my Report) my doubt as to any subsidence. The facts known are against any elevation.

* With regard to Manua, Mr. J. P. Couthouy, of the Wilkes Exploring Expedition for two thirds of its cruise, in his paper on "Coral Formations" (p. 50 of Proc. Bost. Soc. Nat. Hist., Jan. 1842) reported the occurrence of fragments of corals at a height of 80 feet "on a steep hillside rising half a mile inland from a low sandy plain." I was not on Manua. I found on Upolu fragments of coral-limestone and shells in the tufa of a tufa-cone at a height of 200 feet, which had evidently been carried up by the erupting action of a slightly submerged vent. ('Report,' p. 328.) The facts on Manua need further study.

Savaii, the largest island of the group, is a gently sloping volcanic mountain, much like its namesake, Hawaii, in its features, with lavas looking as if not long out of the fire.   It has a broad reef for only 6 or 7 miles of its east shore; elsewhere, on the east and north-east sides, the reefs are fringing or wanting; and on the southern and western sides mostly absent.   No evidence of elevation, and nothing certain as to subsidence, has been reported from the island.

The large Feejee group bears abundant evidence of subsidence in its very broad reef-grounds, barrier islands, and atolls. Fringing-reefs, or barriers with very narrow channels, occur about some of the islands of the group; but in view of the facts that have been stated, these are useless as evidence either way.

Thus the conclusions as to the changes of level about these large Pacific groups south of the equator are not far from Darwin's, although fringing-reefs and the volcanic character of the island are thrown out of consideration, and other conditions exist of varied interpretation.

But cases of actual elevation occur in the Central Pacific about several smaller islands, as proved by *elevated* coral-reefs. These occur in the Austral and Hervey Islands south and south-east of Tahiti, and in the Tonga or Friendly Islands. In none of these, however, thus far reported is the elevation over 300 feet : and the amount varies greatly in adjoining islands of the same group, *some affording proof of no elevation.* Hence only local changes of level, not a general elevation, can be inferred.

To the north of the equator, at the Sandwich Islands some elevated reefs occur; but the amount of elevation is small, and is not general in the group.   Moreover, the reefs are small, where any occur; and the largest island of the chain, volcanic Hawaii, the easternmost, is mostly without reefs, as well as the larger of the westernmost islands, Kauai, which has partly bold and indented shores.

13. To give a more adequate view of the changes of level, or the evidences bearing on the subject, along the " limits " of the central area of subsidence, I mention some additional facts.

Tahiti is the large eastern island of the Tahitian group. To the *westward,* the islands (1) decrease in size; (2) increase greatly in relative breadth of reef-grounds; (3) become deeply indented in shores, as explained; and (4) include an atoll, Tubuai, as one of the last two of the chain.   While the reef of Tahiti proves comparatively little subsidence at that end of the group, and its reefs and channels are extensive enough to make the proof good, the other islands indicate, on the Dar-

winian theory, that the subsidence increases much in amount westward. The western end of the chain is about a degree nearer the equator than the eastern.

In the Samoan Islands, the largest island, Savaii, is the westernmost; and from there the islands decrease in size *eastward*, and end in an atoll, Rose Island. The group is like Tahiti in gradation as to increase of subsidence, but the direction is the reverse; and this fact points apparently to a much deeper area between them *. Moreover, although such broad barrier-reefs as those of Raiatea and Bolabola do not occur in the Samoan group, bold shores do in Tutuila and Manua, and indicate the participation of these islands in the subsidence, notwithstanding their contracted reefs. Further, the reef of Upolu is broad enough to be proof of little change in the region of that island; and there was little, probably, at Savaii, the larger island west of it. The evidence of increased subsidence *to the eastward* is strong, and narrowness of reef is no objection to it.

At the Sandwich Islands the case is similar and yet different; similar in the fact that the largest island of the chain, Hawaii, makes one of its extremities, the eastern, and a series of coral-islands the other—the whole length being 2000 miles; but different in that *no great reef exists* about the shores of either of the eastern islands to *prove* that the subsidence there was small or none. The elevated reefs are only a local phenomenon, and do not prove the absence of subsidence during the era preceding the elevation.

But we have other evidence of importance, derived from soundings about the group by the ' Challenger ' in 1875 and the ' Tuscarora ' in 1874, 1875. These soundings show that the deep-sea area of 3000 to 4000 fathoms comes up quite closely to the eastern end of the chain. It was found within 300 miles of north-eastern Hawaii and 250 of south-western, and within 80 miles of north-eastern Oahu; and a sounding but 125 fathoms less than 3000 was obtained by the ' Challenger ' within 40 miles of eastern Hawaii (or half its diameter). To the westward, along the north side of the chain, the deep-sea area appears to be two or three times more distant, according to the ' Challenger ' results; the condition on the south side is uncertain. It would seem from the great depth near Hawaii, that the region of this great island, although it is now actively *volcanic* and *has little growing coral* about it, had undergone more subsidence than the coral-reef end of the chain, and

* The distance between the remote extremities of these two groups is nearly 2000 miles, and the interval between the nearer over 800 miles.

that its height and steepness of submarine slopes are due to the fact that its outflows of lava have kept ahead of the subsidence, and also built up nearly 14,000 feet above the sea.

This height is large, but the mean pitch of the sides of the volcanic mountains of the island is between 5° and 7° 45′ ; and hence it is only the height which successive outflows should have produced over a vent at the sea-level; and it may be that the accumulation above tide-level has been made since the supposed subsidence ceased.   The depth of 2875 fathoms found by the ‘Challenger’ 40 miles east of Hawaii shows a mean submarine slope to that point of 4° 30′, as if here also was a slope made by flowing lava.   But more soundings are needed to prove that the slope is a gradual one.

14. The facts reviewed show *the uncertainty of evidence* as to little or no subsidence, or as to recent elevation, from (1) narrow reefs, or from (2) the volcanic character of islands, and leave untouched the evidence of actual subsidence from the features of barrier- and atoll-reefs and from deeply indented coasts.

15. After the above considerations, it is clear that the theory of subsidence meets well the facts as to the varying extent of reef among reef-bordered high islands.   According to it, (1) steepness of submarine slope may characterize the side of a barrier-reef (as well as of an atoll) fronting east or west, north or south, as is true of high islands ; but it is least likely to occur in the direction of the trend of the island or group, or that of current drift.   (2) Fringing-reefs, or no reefs, may characterize one side, that of bold bluffs, and wide barriers the opposite.   (3) The barrier-reef may be made on the submarine slopes of the land, or on a broad plateau or lowland area between ranges of elevations, one or both of which have disappeared in the subsidence.   (4) By continued subsidence, the side having a fringing-reef or no reef, may, later in the subsidence, be that of a very broad barrier-reef, because of the form of the surface of the subsiding land ; and *vice versâ*.

The third of these propositions is well illustrated by the facts from the Maldives, as reported by Darwin.   On account of its importance I add an illustration from the Feejees.

The great reef-grounds along the north-west sides of the two large Feejee islands, Vanua Lebu and Viti Lebu, do not indicate a subsidence proportional to their width.

Each of these islands is over ninety miles long, and together the trend is north-eastward*.   The north-western

* A map of the Feejee group is contained in my ‘Corals and Coral Islands,’ and of larger size in Wilkes’s ‘Narrative of the Expedition.’

reef-grounds are 10 to 25 miles wide ; while on much of
the south-east side of each island there is (according to the
Wilkes chart) only a fringing-reef.   The true explanation of
the great width is found, not in the amount of the subsidence
alone, but largely in the existence there of a broad area of
submerged land at relatively small depths.   This inference is
sustained by the fact that the outer barrier-reef, after being
simply a barrier-reef for 125 miles with but two rocky islets
in its course, becomes in the same line westward for seventy
miles, a range of high narrow reef-bordered islands (called the
Asaua Range), and then bends around southward through
other rocky islands to meet the west end of Viti Lebu.   The
reef-grounds have thus a chain of islands as their boundary
for a length of 100 miles, and simply a barrier-reef with two
rocky islets for the rest of the line (125 miles).

The following figure illustrates in a general way the above
condition.   It is a section across the reef-grounds, *i k*, and
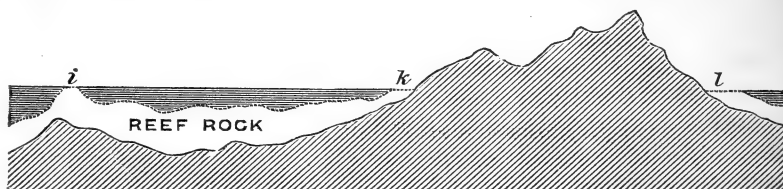
the outer barrier-reef *i*, with a fringing reef at *l* ; and sup-
posing it to have a rocky island at *i*, it represents a section
(further to the south-west) across the reef-grounds and the
outer range of islands.   The reason for the existence of only
fringing-reefs for much of the south-east side has not been
particularly investigated.

16. Local elevations within the sinking area are not evi-
dence against the Darwinian theory of subsidence.   Local
disturbances and faults, as both theory and the rocks of the
continents show, are almost necessary concomitants of a
slowly progressing change of level.   Besides this, igneous
conditions beneath a region are a common source of local
displacements.   Such displacements are therefore to be looked
for in the tropical oceans, since the various high islands are
volcanic, and the coral-islands probably have a volcanic base-
ment ; and, moreover, the islands are not unfrequently shaken
by earthquakes.   The causes of local displacement by either
method would not necessarily interfere with any secular
change of level in progress.

17. The shore-platform of an atoll, or the " flat," as called
by Darwin, situated just above low-tide level, consists usually

of the true reef-rock, or the rock made by under-water con-
solidation ; and its height is determined chiefly by the height
of wave-action, its general surface being produced by the
chiseling-effect of the in-flowing waters. When found above
its normal level, it is probable evidence of an elevation ; and
on this kind of evidence the conclusion rests in several of the
cases of supposed elevation which I mention in my Report.
The width of the platform and its evenness of surface vary
with the height of the tides. When the tides are 5 to 6 feet,
the platform is narrow, more cut up by channels and less
even in surface. After an elevation, if but a foot or two in
amount, the surface of the platform becomes restored finally
for a large part of its surface to its normal level, and gentle
slopes may connect the newer and older portions. But if
the rise of an atoll is 10 feet, great degradation takes place
along the lifted edge of the reef, which may end in reducing
the elevated coral-barrier to a wall with numerous channels
and broad spaces opening through to the lagoon, as observed
by the writer (from ship-board) on the south side of Dean's
Island*.

18. The differences in the *kinds of coral-rocks* should be
understood (as the recent discussions of Darwin's theory
have shown) in order to appreciate the structural facts that
bear on changes of level. The *beach-made* rock is of *above-
water* consolidation (through calcareous deposition about the
grains as evaporation takes place), and is porous, often oolitic;
and if a conglomerate, it consists mostly of worn masses.
The rock made of drifted sands is similar. But the true

---

* Our cruise took us from the Paumotu atolls to Australia, and there,
the sandstone bluffs making the capes of Port Jackson gave me my first
understanding of the atoll's " shore-platform." This bluff has its " shore-
platform," 50 to 150 yards wide, bare at low tide ; it was the lower
layer of the sandstone, a regularly jointed rock, lying like a loosely laid
pavement. It seemed strange that it was able to keep its place in the
face of the breakers. But the first waters of the in-coming tide swelled
quietly over it, and served to shield it from the plunging waters of the
latter part of the flow ; the waves, therefore, found nothing to batter
against short of the base of the bluff.

A view of Deans Island from the south is given in Wilkes's Narrative,
i. p. 342; it fails only in not giving a nearly even top line to the columns.
The view on p. 334 looks as if representing another example of similar
erosion. But, as the text implies, the group of masses of coral-rock was
made by the artist by bringing into a single view the blocks that had
been observed in an isolated way over the platforms of atolls. The size
and shapes of the blocks are exaggerated. But, although isolated, such
blocks are often so united to the coral-platform that they appear to be a
constituent part of it (my ' Report,' p. 61) and suggest the question
whether they may not be remnants of an overlying layer elsewhere
removed.

coral-reef rock is of *under-water* consolidation, and is usually very compact, like an ordinary limestone ; and if a conglomerate, it is commonly a breccia, and sometimes a very coarse breccia.   Some masses of it lying on the shore-platform of Paumatu atolls (thrown up by storm or earthquake-waves), 100 to 2000 cubic feet in contents, consisted of single pieces of massive corals—*Astræas, Porites,* &c. ; and others were an agglomeration of fragments of corals.   The fine-grained or impalpable kind made from coral-mud may have few or no fossils, and be a magnesian limestone.

Another variety of the coral-reef rock, made in lagoons and sheltered channels, has the corals in the position of growth ; and when formed of branching corals, the spaces among the branches are often but partly filled.   It is a weak rock ; and the islets thus made in lagoons and inner channels are sometimes overturned by the heaviest of waves ; and rising banks (as the experience of the Wilkes Expedition proves) may be crushed beneath the keel of a passing vessel.

Owing to the different modes of origin of the beach-made rock and the true coral-reef rock, the occurrence of the former underneath the latter would be evidence of subsidence.

Deep borings in atolls with circular drills that would give a 6-inch core would supply evidence as to the existence or not of beach-made coral-rocks at levels below the surface. They would also determine the depth to which true modern coral-reef rock extends and the nature of the underlying beds, whether calcareous, volcanic, or of any other kind.   This is hence a sure method for obtaining a final decision of the coral-island question, and should be tried[*].

---

[*] The Wilkes Expedition carried out apparatus for boring.   It was put into inexperienced hands, as Commodore Wilkes states in his ' Narrative' (iv. pp. 267, 268), and at a trial with it on Aratica (Carlshoff Island) in the Paumotus, it became broken and useless at a depth of 21 feet. Moreover, the granulated material brought up afforded no satisfactory evidence as to the kind of coral-rock encountered.   The statement in the ' Narrative' that " the low coral-islands, as far as they have been investigated, both by boring and sounding, have shown a foundation of sand, or what becomes so on being broken up," has been quoted and made more of than the facts warrant.   The " soundings" reached only the sands of the sea-bottom ; and the " boring," if it found sand at bottom, proved only that the beach-made rock may exist at the 21-foot level, in which case a small subsidence would be indicated.

Commodore Wilkes says on p. 269 of the same volume :—" The elevated coral-islands which we have examined exhibit a formation of conglomerate composed of compact coral and dead shells, interspersed with various kinds of corals, which have evidently *been deposited after life has become extinct.*   A particular instance of this was seen at the island of Metia, and the same formation was also observed at Oahu." As the corals of a

19. *Elevated* coral-reefs afford an opportunity to search for layers of beach-made rock underlying true reef-rock ; and also, if over 120 feet in height, to ascertain directly the character of the rocks below this level.

The elevated atoll, Metia, 75 miles north-east of Tahiti, whose maximum height (according to the measurement of officers of the Wilkes Expedition) is 250 feet, I have described as consisting of the true coral-reef rock. My examinations were made on the west side, where it presents a vertical front to the water. The white compact limestone was, in some parts, almost destitute of fossils, or had only an occasional mould of a shell or fragment of coral* ; and in others it was a fine or coarse coral-breccia. My notes written out at the island include the statement that " large masses of corals make some lower layers." This observation, though not as complete as I now see that it should have been, favours the conclusion that the thickness of the reef-rock is at least twice as great as the depth to which reef-corals grow, in which case the elevated reef is proof of a subsidence of 120 feet or more.

The island is so near the route to Tahiti that the doubt which remains could be readily removed.

20. The subsidence indicated, according to the Darwinian theory, by atolls and barrier-reefs was *actual*, not apparent subsidence attributable to change of water-level. The difference in its amount between the Central-Pacific area of subsidence and its limits (§§ 10, 11, above), the gradation or variation in amount of subsidence along chains of islands (§§ 10, 12, 13), and the local character of elevations, like those of Metia, Mangaia, and many others, are proofs on this point.

The preceding explanations have prepared the way for the consideration of the arguments urged against the Darwinian theory, to which I now pass.

[To be continued.]

conglomerate, whether consisting of rounded masses or angular, are " deposited after life has become extinct," no inference as to the particular kind of coral-rock intended can be drawn from the remark. From my knowledge of the island I presume he meant the ordinary breccia conglomerate of the reef-rock, which is one of the kinds of coral-rock of the elevated island. Commodore Wilkes himself made no examination of the rock or special study of coral-islands, as might be inferred from his theoretical views on p. 270 of volume iv. His ' Narrative' was to a considerable extent made up from the journals of his various officers.

* It was this compact rock, white, flint-like in fracture, clinking under the hammer, that was found on analysis by B. Silliman to contain 38·07 per cent. of magnesium carbonate.

XVIII. *On the Specific Refraction and Dispersion of Light by the Alums. By* J. H. Gladstone, *Ph.D., F.R.S.*[*]

IN the *Comptes Rendus* of November 17, 1884, there appears a paper by M. Charles Soret, in which he gives the refractive indices of a large number of crystallized alums. They were determined by the method of total reflection, and are measured for the lines of the solar spectrum *a*, B, C, D, E, *b*, F, and G. As at the same time M. Soret gives the specific gravity of the specimens examined, it is easy to calculate out the specific refraction and dispersion of these crystals, and it occurred to me that the observations might serve three purposes. They might test the truth of certain physical laws ; they might arbitrate between myself and Kanonnikoff as to the refraction-equivalent of certain metals ; and they would give values for indium and gallium, which have not hitherto been obtained. Through the kindness of M. Soret I have received his full paper[†], with some further information, and observations on three additional alums not yet published, viz. the Rubidium Gallium, Rubidium Indium, and Cæsium Chromium alums.

In order to bring M. Soret's figures into comparison with my own, which are always based on the line A of the spectrum, it was necessary to reduce his figures accordingly. This was easily done, as the line A falls short of *a* by almost exactly the same amount as that one falls short of B. The following table gives the specific gravity of the selected crystals ; the refractive indices (μ) for A calculated to the fourth place of decimals, and also those for G ; the specific refraction for A,

i. e. the index -1 divided by the density, $\left(\dfrac{\mu_A - 1}{d}\right)$; the specific dispersion A to G, *i. e.* the difference between the specific refraction of these two lines, $\left(\dfrac{\mu_G - \mu_A}{d}\right)$; and the refraction-equivalent for A, *i. e.* the specific refraction multiplied by the atomic weight, $\left(P\dfrac{\mu_A - 1}{d}\right)$. The general formula of the alums is R_2, Al_2, $4\,SO_4$, $24\,H_2O$; the aluminium being replaceable by indium, gallium, chromium, and iron.

Alum.	Specific gravity.	$\mu_A.$	$\mu_G.$	$\dfrac{\mu_A-1}{d}.$	$\dfrac{\mu_G-\mu_A}{d}$	$P\dfrac{\mu_A-1}{d}.$
Ammonium Aluminium..	1·631	1·4542	1·4692	·2784	·0093	252·23
Sodium „ ...	1·667	1·4342	1·4480	·2604	·0083	238·52
Methylamine „ ...	1·568	1·4496	1·4636	·2867	·0090	267·68
Potassium „ ...	1·735	1·4516	1·4661	·2603	·0083	246·81
Rubidium „ ...	1·852	1·4513	1·4662	·2437	·0080	253·69
Cæsium „ ...	1·961	1·4536	1·4682	·2313	·0074	262·31
Thallium „ ...	2·257	1·4914	1·5108	·2177	·0086	278·34
Ammonium Chromium...	1·719	1·4781	1·4959	·2781	·0104	265·94
Potassium „ ...	1·817	1·4754	1·4931	·2616	·0098	261·22
Rubidium „ ...	1·946	1·4756	1·4932	·2444	·0090	266·69
Cæsium „ ...	2·043	1·4753	1·4928	·2326	·0086	275·50
Thallium „ ...	2·386	1·5158	1·5381	·2161	·0092	286·90
Ammonium Iron	1·713	1·4783	1·4998	·2792	·0126	269·15
Potassium „	1·806	1·4757	1·4960	·2634	·0112	265·03
Rubidium „	1·916	1·4763	1·4970	·2486	·0108	273·21
Cæsium „	2·061	1·4772	1·4984	·2315	·0103	275·95
Thallium „	2·385	1·5155	1·5411	·2161	·0108	288·85
Rubidium Indium.........	2·065	1·4586	1·4740	·2221	·0074	269·63
Rubidium Gallium	1·962	1·4606	1·4758	·2348	·0077	264·43

Messrs. Topsoe and Christiansen[*] have also published the refractive indices of three alums for the lines C, D, and F ; and as they have given the specific gravity, their observations are available for the same purpose. The index for A has been calculated from these data.

Alum.	$\mu_A.$	$\mu_C.$	$\dfrac{\mu_A-1}{d}.$	$P\dfrac{\mu_A-1}{d}.$
Potassium Iron Sulphate	1·4751	1·4783	·2597	261·37
Ammonium Iron Sulphate	1·4789	1·4821	·2786	268·56
Potassium Aluminium Seleniate	1·4748	1·4773	·2409	272·98

How far do these figures support the former conclusion, that a salt has the same specific refraction whether in a solid form or in solution ?

For this purpose determinations were made of the refraction for A in aqueous solutions of the first two alums in M. Soret's list. Deducting the amount due to the solvent, the following values were arrived at :—

	Dissolved.	Crystallized.
Ammonium Aluminium alum . .	·2780	·2478
Sodium Aluminium alum . . .	·2613	·2604

* "Krystallografisk-optisk Undersoegelser," *Det K. Danske Viden-skabernes Selskabs Skrifter*, 1873, p. 622.

M 2

These numbers are as close as two different specimens of the same salt, even if they were in the same condition, are likely to be. It did not seem worth while to obtain additional proof of a law which has already been established by many cases ; not only by my previous observations, but also by those of Topsoe, Bedson, and Kanonnikoff.

Do these figures confirm the law that the refraction-equivalent of a compound body is the sum of the refraction-equivalents of its components?

The alums may be regarded as a compound of the sulphates of two metals of different kinds with 24 molecules of water. Now water in the uncombined state has the refraction-equivalent of 5·926 ; and in regard to the sulphates we have the following data :—

Ammonium sulphate, $(NH_4)_2SO_4$, 39·3. The mean of five determinations made by myself gives 39·35 * : Kanonnikoff gives 39·27 †.

Sodium sulphate, Na_2SO_4, 26·6. Kanonnikoff gives 26·02.

Methylamine sulphate, $(NCH_6)_2SO_4$, 54·5 ; *i. e.* ammonium sulphate with the addition of $2 CH_2$, or 15·2.

Potassium sulphate, K_2SO_4, 32·4. The mean of five determinations gave me 32·6 : Kanonnikoff gives 32·22. It may be estimated at 32·3 from Topsoe and Christiansen's determinations of the crystallized salt.

Rubidium sulphate, Rb_2SO_4, 41·3. This is Kanonnikoff's determination, which I prefer to my own made in 1869.

Cæsium sulphate, Cs_2SO_4, 55·3. Also Kanonnikoff's.

Being not content with my old observations on the sulphates of the trivalent metals, I have recently determined them afresh, with the following results :—

Aluminium sulphate, $Al_2(SO_4)_3$, 70·5.

Chromium sulphate, $Cr_2(SO_4)_3$, 82·5 ; the result of old and new observations.

Ferric sulphate, $Fe_2(SO_4)_3$, 89·1 ; the mean of old and new observations.

It is evident that on adding together

Ammonium sulphate . .	39·3
Aluminium sulphate . .	70·5
24 Water	142·2
We obtain	252·0

In this way the second column of the following table has been calculated :—

* Four of these are given in my paper in the Phil. Trans. 1869, p. 9.
† Journal of the Russian Physico-Chemical Society, 1884, p. 119.

Substance.	Refraction-equivalent.		
	Calculated.	Observed, and reduced to A.	
		Soret.	Topsoe and Christiansen.
Ammonium Aluminium alum......	252·0	252·2	
Sodium ,, ,, ...	239·3	238·5	
Methylamine ,, ,, ...	267·2	267·7	
Potassium ,, ,, ...	245·1	246·8	
Rubidium ,, ,, ...	254·0	253·7	
Cæsium ,, ,, ...	268·0	262·3	
Ammonium Chromium alum	264·0	265·9	
Potassium ,, ,, ...	257·1	261·2	
Rubidium ,, ,, ...	266·0	266·7	
Cæsium ,, ,, ...	280·0	275·5	
Ammonium Iron alum...............	270·6	269·1	268·6
Potassium ,, ,, ...	263·7	265·0	261·4
Rubidium ,, ,, ...	272·6	273·2	
Cæsium ,, ,, ...	286·6	276·0	

The agreement between the results calculated and found is as near as might be expected, except in the case of cæsium. It confirms the general law, as the variations only in one instance amount to as much as 1 per cent., and are sometimes plus and sometimes minus. There is little doubt that the cæsium, in one set of observations or the other, was impure : an old determination of mine, from the chloride, would give figures lower than Soret's.

Do these data afford us the means of determining the refraction-equivalents of the elements with more exactness than heretofore ? It is evident that in the series of aluminium alums the metal having the smallest refraction-equivalent is sodium, and that the rest follow in the order—potassium, ammonium, rubidium, methylamine, cæsium, and thallium ; the same order is preserved in the chromium and iron alums as far as they extend. This agrees with the order previously determined both by myself and Kanonnikoff ; but when we look more closely into the matter it is evident that the figures are not very exact. Thus, in the aluminium series the difference between $2NH_4$ and $2K$ is 5·42 ; but in the chromium series it is only 4·72, and in the iron series 4·12, or 7·19 according to Topsoe. The values of potassium deduced from this would vary considerably : assuming the value of NH_4 to be 11·1, it might be either 8·4, 8·7, 9·0, or 7·5 ; which are wider differences than between my old estimation, 8·1, and Kanonnikoff's recent independent determination, 7·75. This will not be wondered at when it is remembered that all expe-

rimental errors are accumulated on these residual numbers. The optical determinations of Soret are so uniform and exact as to inspire the greatest confidence; but he is not satisfied with the specific gravities. Errors may also arise from impurity of the salt, or want of homogeneity in the crystal. An aqueous solution is probably a more uniform substance than a hydrated crystal, and better fitted for the purpose of determining optical equivalents.

On this account any determination of the refraction of indium and gallium made from these alums must be open to considerable question : the rubidium compounds of these metals, however, are believed by Soret to be fairly pure salts, and we can compare them with three other alums of rubidium. It would appear from the first table that indium has the value of aluminium $+8\cdot0$, or of chromium $+1\cdot5$, or of iron $-1\cdot8$; and, similarly, that gallium has the value of aluminium $+5\cdot4$, or of chromium $-1\cdot1$, or of iron $-4\cdot4$. Now aluminium sulphate has already been estimated at $70\cdot5$, chromium sulphate at $82\cdot5$, and ferric sulphate at $89\cdot1$, while the value of SO_4 is held both by Kanonnikoff and myself to be $17\cdot0$. We may therefore deduce the following refraction-equivalents :—

Aluminium	.	.	.	.	9·7
Chromium	.	.	.	.	15·7
Iron	.	.	.	.	19·0

and :—

	From Aluminium Salt.	From Chromium Salt.	From Iron Salt.
Indium	17·7	17·2	17·2
Gallium......	15·1	14·6	14·6

From the mean of the above the following constants may be derived :—

	Atomic weight.	Specific refraction.	Refraction-equivalent.
Indium	113·6	·1532	17·4
Gallium.................	69·8	·2120	14·8

These numbers can only be looked upon as approximate.

Turning to the matter of dispersion.—It has already been shown that the refraction-equivalent of an alum is the sum of the refraction-equivalents of its constituents for the line A. If this law holds good equally for the more-refrangible part

of the spectrum, it follows that the dispersion-equivalent $(P\frac{\mu_G-1}{d} - P\frac{\mu_A-1}{d}$, or, which is the same thing, $P\frac{\mu_G-\mu_A}{d})$ of an alum is the sum of the dispersion-equivalents of its constituents. The data by which this can be tested are not so numerous or so trustworthy as in the former case, but the following may be accepted.

The dispersion-equivalent for water . . . . 0·212

"   "   aluminium sulphate 2·40

"   "   ammonium sulphate 1·33

"   "   sodium sulphate . 0·83

from which may be deduced :—

Dispersion-equivalent of	Calculated.	Observed.
Ammonium alum............	8·82	8·40
Sodium alum	8·32	7·65

Though these figures are tolerably accordant, it will be seen that those in the first column are decidedly higher than those deduced from Soret's measurements. The differences are about 5 and 8 per cent. respectively ; but there are known sources of error in experiment which may affect the first place of decimals.

The dispersion-equivalents of the different alums may be thus tabulated :—

	Dispersion-equivalents of the Alums.				
	Alumi-nium.	Chromium.	Iron.	Indium.	Gallium.
Ammonium salt	8·40	9·91	12·11		
Sodium "	7·65				
Methylamine "	8·47				
Potassium "	7·92	9·73	11·31		
Rubidium "	8·36	9·87	11·86	8·98	8·73
Cæsium "	8·44	10·15	12·28		
Thallium "	10·98	12·13	14·45		

It is evident at once :—

First. That the differences due to the replacement of one metal by another are very considerable ; more considerable in proportion than the differences in the case of the refraction-equivalents.

Secondly. That the different compounds of the alkalis pre-

serve the same order, and nearly the same proportion, in the aluminium, chromium, and iron series : the order is thallium far the highest, methylamine, cæsium, ammonium, rubidium, potassium, and sodium lowest.   This is the same order which may be deduced from old observations on sulphates, nitrates, chlorides, and acetates.

Thirdly. That the order of the other metals is iron far the highest, chromium, indium, gallium, and aluminium lowest. This is also in accordance with observations on the simple sulphates of those previously examined.

Our knowledge on this part of the subject is not yet sufficiently advanced to determine the dispersion-equivalents of the separate elements.

XIX. *On the Bleaching of Iodide of Starch by means of Heat.* By CHARLES TOMLINSON, *F.R.S.*[*]

THE bleaching of iodide of starch by means of heat forms a pretty experiment.   An aqueous solution of iodine and one of starch may be mingled together in a test-tube, when the well-known densely blue colour is produced.   If the tube be held over the flame of a spirit-lamp, the blue gradually becomes paler and paler, and disappears long before the liquid has reached the boiling-point.   If the hot tube be now plunged into cold water, the blue colour immediately reappears, starting up from the bottom of the tube, where the reduced temperature is first felt, and quickly spreading through the liquid up to the surface.   The colour returns, but of course more slowly, if the tube be left to cool in the air.

Thénard, in noticing this experiment upwards of half a century ago, remarked that it is, " sans contredit, la plus remarquable de toutes les propriétés de l'iodure " [†].

It is surprising what a large number of papers have been written on this apparently simple experiment.   Gmelin (Handbook, Cavendish Society's Translation, xv. p. 99) has collected most of them down to 1862 ; and they exhibit various contradictions.   For example, some writers maintain that the iodine and the starch form a definite chemical compound, others describe it as a mechanical mixture ; some maintain that iodic and hydriodic acids are generated on heating the compound, others deny that this is the case ; some say that the blue liquid may be heated many times in a sealed tube and yet recover its colour on cooling ; this also is denied.   Such statements as these led Professor Miller, in the ' Text-book on Inorganic Chemistry ' that he wrote shortly before his death, to remark

[*] Communicated by the Author.
[†] My copy of Thénard's *Traité de Chimie* is a Brussels reprint, dated 1836 (vol. ii. p. 157).

(1871, p. 136) that " the cause of this change of colour is not known."

Some writers, as quoted by Gmelin, maintain that if the iodine which evaporates in boiling be expelled by blowing air into the vessel, the iodide of starch remains colourless after cooling, but if it can reabsorb the iodine-vapours on cooling the colour is restored. A sufficient answer to this is that the colour begins to reappear at the bottom of the tube long before the vapours at the upper part can possibly be reabsorbed. The vapours may even be blown away and yet the colour reappear.

The usual mode of accounting for the discoloration is that given in Watts's ' Dictionary of Chemistry,' under STARCH, v. 1868, p. 410:—" The liquid may be decolorized by ebullition, whereby the iodine is volatilized ; if, however, the boiling be not continued for a sufficient time to volatilize the whole of the iodine, the blue colour reappears as the liquid cools."

This statement is but partially true ; for the colour disappears long before the boiling-point is reached, and it does not account for the fact that when the liquid is apparently permanently bleached and allowed to get cold, the addition of a few drops of solution of chlorine will restore the blue colour.

In examining this subject experimentally, the difficulty seemed to lie in the multitude of explanations rather than in any inherent difficulty belonging to it. My first care was to determine the temperature at which the bleaching takes place. For this purpose, fifteen grains of iodine were treated with half-a-pint of distilled water, and five grains of each of four varieties of starch were rubbed up and then boiled with about an ounce of distilled water.

1. One ounce of solution of starch crisp from maize was mixed with one ounce of the iodine solution in a small globular flask and heated over the flame of a spirit-lamp. The colour entirely disappeared at from 150° to 160° Fahr. (65° to 71° C.). Left to cool in the air of the room the colour began to return at 120° F. (49° C.), and the full colour was restored at 70° F. (21° C.). The flask was heated a second and a third time, with nearly similar results.

2. A solution with rice-starch became paler at 105°, much paler at 115°, pale at 120°, and the colour entirely disappeared at from 135° to 140°. The flask was plunged into cold water, when the solution became reddish at 135°, purple at 100°, violet at 80°, and blue-violet at 70°.

3. With sago-starch the colour became lighter at 110°, pale blue at 120°, pale at 140°, and was bleached at 150°. In cold water the colour returned at 130°, at 85° it was full blue, and at 80° quite opaque, like ink.

4. The mixture with potato-starch was of a blue-black

colour. At 105° it became pale, at 125° of a light red, and at 140° entirely bleached. In cold water it became reddish a little below 140°; at 120° a purplish tinge came over the red; at 90° the colour was purplish, at 80° violet, at 78° reddish violet by transmitted and blue by reflected light.

A fifth variety of starch, namely that used for domestic purposes in my house, was taken ; but this was soon recognized as potato-starch by the method of Gobley (*Journ. de Pharm.* for April 1844), in which various specimens of starch, in watch-glasses, are arranged on a plate around a central watch-glass containing iodine, the whole being covered with a bell-glass. I found that some of the specimens, namely such as were slightly moist, became coloured by the iodine vapour in the course of a few minutes ; others in an hour or so, according as they absorbed moisture, there being no action with dry samples. If known samples are first acted on, the colours assumed by them may serve to determine other unknown specimens.

The four varieties of starch above referred to were made up into thin and thick solutions, the thin containing five and the thick ten grains of starch in about half-an-ounce of water. Equal quantities of the starch solutions were severally mixed with equal quantities of the iodine solution, thereby producing very dark blue or blue-black compounds. Each variety was heated in a test-tube over a spirit-lamp flame and boiled during two minutes, and then cooled by plunging the tube into cold water. The colour was not in any case reproduced during the cooling ; but on the addition of a few drops of an aqueous solution of chlorine the colour was restored in each case, but with very different degrees of intensity ; for while in the case of potato- and rice-starch the blue was almost as intense as before the boiling, it was faint in the case of maize or absent in that of sago, or exhibited but a mere trace in several trials. A specimen of arrowroot also behaved like the sago. Hence it seems that different kinds of starch act on iodine with different degrees of intensity, in character not like a chemical compound so much as, according to Liebig and others, a precipitation of the finely divided iodine on the surface of the granules of the starch.

M. Personne (*Comptes Rendus* for 1872, p. 617, in answer to M. Duchaux, p. 533 of the same volume) refers to a statement of his in the *Comptes Rendus* for 1861, in which he regards iodide of starch, not as a chemical compound, but produced by the fixation of iodine on starch in the same manner as a colouring-matter is fixed on a tissue. The blue compound, he says, must be regarded as a dye, not a true lake[*].

---

[*] Puchot (*Comptes Rendus*, 1883, p. 225) has noticed that albumen poured on iodide of starch suspended in water causes the colour to disappear. Whey (*petit-lait*) has a similar effect. Here, again, I found

It is evident from the preceding details that, during the heating of the tube containing the so-called iodide of starch, the solvent power of the liquid for iodine increases with the temperature, and if the tube be watched at the moment when the last trace of colour disappears, the tint of iodine in solution becomes apparent ; but this aspect soon disappears, not only on account of the small quantity of iodine present and the rapidly increasing solvent power of the liquid as the temperature rises, but also from the loss of iodine in the steam which escapes from the mouth of the tube. This view of the case is supported by the fact that if boiling solutions of starch and iodine be mingled no colour is produced ; for at this high temperature the starch and the iodine seem to be dissociated and incapable of mutual action. This appears to be what is meant by Brücke (as stated in the Chemical Society's Abstracts for 1884, p. 576), who makes the bleaching to depend on the affinity of warm water for iodine being greater than that of cold water.

Thus far the reasoning seems to be justified by the facts ; but the restoration of the colour on the addition of chlorine, apparently after all colour had been destroyed, remains to be accounted for. In such case the small quantity of iodine that remains after the boiling seems to be disguised under the form of hydriodic acid, formed partly, as Thénard suggested, at the expense of the starch ; and the action of the chlorine is to set free a minute quantity of iodine, sufficient, however, for the starch to restore the blue colour. The fact just given, that boiling solutions of the starch and iodine may be mingled without the production of colour further supports the above view ; nor does the colour appear when the tube has become cold ; but the addition of a few drops of chlorine solution immediately starts the colour, or if to any of the tubes containing the cold bleached solution a few drops of nitrate-of-silver solution be added, a faint indication of the presence of hydriodic acid is obtained.

The conclusions arrived at seem to be:—

1. That the blue colour disappears in consequence of the dissociation of the iodine and the starch under the action of a high temperature.

2. That when the liquid is apparently permanently bleached, and yet the colour is restored by the action of chlorine, a minute quantity of iodine is present under the form of hydriodic acid.

---

the effects to vary with different kinds of starch, the blue colour disappearing more quickly in the case of rice- than with potato-starch. Casein (cheese, for example) causes a precipitation of the blue compound upon itself, leaving the liquid clear above. Milk also bleaches, apparently from the presence of casein.

XX. *The Production of Monochromatic Light, or a Mixture of Colours, on the Screen.* By Capt. W. DE W. ABNEY, *R.E., F.R.S.**

FOR some time past I have been making experiments on the illuminating power of various sources of light, and it became necessary in some investigations to produce fair-sized patches of different monochromatic, and combinations of monochromatic lights, upon a screen, all other colours being absent. To obtain this result I had recourse to a modification of Clerk-Maxwell's arrangement, as used for colour-mixing. By his plan slits were inserted at different parts of the spectrum as formed by an ordinary spectroscope. These slits were then illuminated by light reflected from a white screen, and the prism was viewed through the slit of what is ordinarily the collimator. The prism was then seen to be coloured
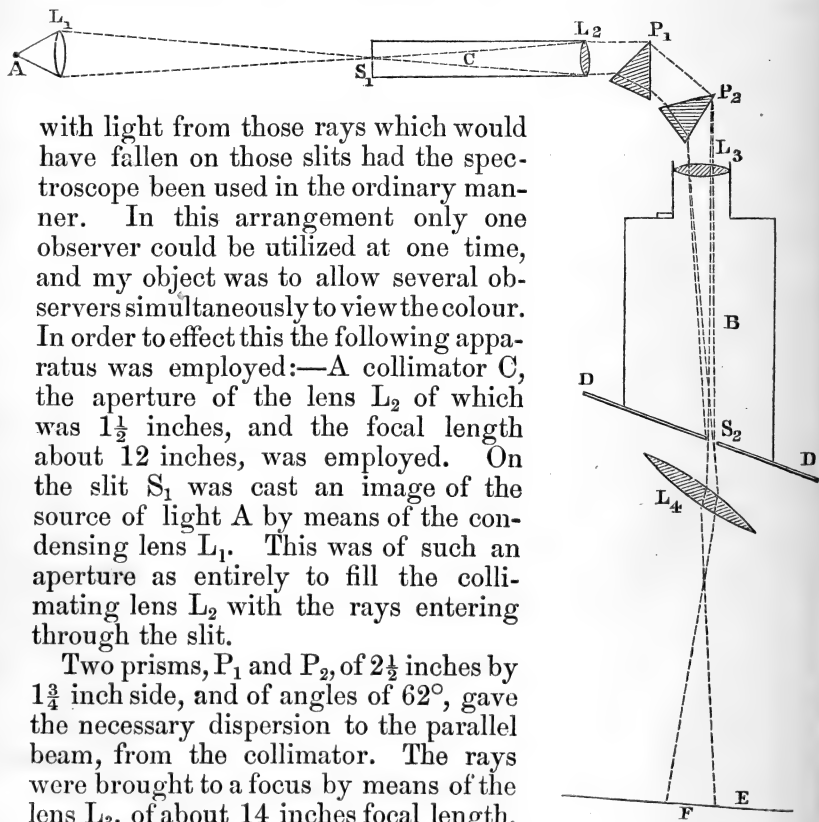
with light from those rays which would have fallen on those slits had the spectroscope been used in the ordinary manner. In this arrangement only one observer could be utilized at one time, and my object was to allow several observers simultaneously to view the colour. In order to effect this the following apparatus was employed:—A collimator C, the aperture of the lens L_2 of which was $1\frac{1}{2}$ inches, and the focal length about 12 inches, was employed. On the slit S_1 was cast an image of the source of light A by means of the condensing lens L_1. This was of such an aperture as entirely to fill the collimating lens L_2 with the rays entering through the slit.

Two prisms, P_1 and P_2, of $2\frac{1}{2}$ inches by $1\frac{3}{4}$ inch side, and of angles of 62°, gave the necessary dispersion to the parallel beam, from the collimator. The rays were brought to a focus by means of the lens L_3, of about 14 inches focal length,

* Communicated by the Physical Society : read June 27, 1885.

on to the screen belonging to a camera, B.   This screen was placed at an angle with the axis of the lens L_3 as shown, so that a fair focus of every visible ray was obtained upon it.   (It may be worth mentioning that a hair placed across the slit or a little particle of dust is a good means of obtaining a focus when Fraunhofer or bright lines are not observable.   The black streak produced by it should be sharp along the whole of the spectrum.)   A card, D D, with a slit S_2 or slits cut in it, replaced the ordinary dark slide, and, by moving it along the spectrum, any colour or colours can be allowed to pass. Before using the apparatus the whole of the spectrum was caused to fall on a convex lens, L_4, of about 24 inches focal length and about 5 inches diameter.   This collected the dispersed beam of light, giving an enlarged image, F, of one surface of one of the prisms on a screen, E.   By placing this lens at an angle with the axis of the lens L_3, the blue and red fringes can be made to disappear almost entirely, and a practically white patch of light is seen on the screen E.

I may say that the lenses used are white flint of medium density and almost colourless, even in great thickness.

When the adjustments are complete, as the slit is moved along the spectrum every patch of colour or colours will successively occupy the same position on the screen and have the same area very nearly.   We thus can have patches of monochromatic light of any colour or combinations of any colours, all other colour being absent.

I have also obtained the same results by substituting mirrors for all the lenses and a reflecting-grating for the prisms; but I do not see any particular advantage in this plan, as the white light is more tinged (with the colour of the metal) than when prisms and lenses of white glass are employed.

When the source of light is the arc light, if an image of the crater of the positive pole be thrown on the slit S_1 of the collimator, the intensity of the light is such (when the slit is fairly open) that the patch of nearly pure light may be made 1 foot square, and yet be sufficiently brilliant to be seen by a fairly large audience, and for an ordinary lecture-room it is very effective.   The mixture of colours to imitate any colour in the spectrum may be shown by placing a narrow slit in a small card in the colour required to be imitated, and fixing in front of it and in contact with it a portion of a cylindrical lens, the axis of the cylinder being of course parallel to the slit.   This throws the image of the particular colour to be observed at one side of the image that would be obtained were the cylindrical lens absent, and any amount of deviation can be given the patch by using the different parts

of the lens. Thus the greater the deviation required the nearer to the margin of the lens the part of it employed should be. In other words, the cylindrical lens acts as a series of prisms of varying angles. To obtain mixtures of colours to correspond to the deviated patch, movable slits, and capable of being narrowed or widened, are placed on each side of the fixed slit. By this plan two patches of light of equal size and equal intensity can be readily produced. When measurements are to be obtained, scales are attached to the various slits, by which any part of the spectrum can be identified ; and the widths of the slits are measured by a gauge.

Since this apparatus was described I have referred to a paper by Helmholtz, which appeared in Poggendorff's *Annalen* in 1855, in which one of the methods he used for the combination of coloured light to produce white light is described. The general principle he adopted is the same as that described above ; but in several important details the latter differs considerably from Helmholtz's apparatus. For instance, the apparatus now described is suitable for the comparison of colour-mixtures with monochromatic light of any colour and for their exhibition on the screen for lecture-purposes, and an illumination is secured which is very largely in excess of that usually obtained. In a paper read before the Physical Society (Phil. Mag. June 1885) Lord Rayleigh shows how a monochromatic image of an external object may be seen by placing a concave lens immediately behind the slit of the spectroscope of such a power as to throw an image of that object on the prism. I have found that by altering the distances apart of the collimating lenses and viewing lens, a monochromatic image of the sun may be thrown on the screen. If such an image be coloured with the light of the blue or violet hydrogen lines, it should be possible to photograph the solar prominences *en bloc.* I may mention that the apparatus as described was employed in two Cantor Lectures at the Society of Arts in the beginning of April, but without describing it in detail.

I am at present engaged in using this apparatus for investigating some phenomena existing in colour-blindness, and obtaining curves of illumination of different lights, and also in some photographic researches. These results are not yet ripe for publication ; but I have thought it might be well to publish the method employed, as it is one of great convenience, and very easily carried out by any one who has a spectroscope and a photographic camera.

XXI. *Mechanical Integration of the Product of two Functions.* *By* WILLIAM SUTHERLAND, *M.A., B.Sc.*[*]

IN a communication to the Royal Society (February 3, 1876), "On an Instrument for Calculating $\int \phi(x)\psi(x)dx$, the integral of the product of two Functions," Prof. Sir William Thomson has shown how, by the use of Prof. James Thomson's disk, globe, and cylinder integrating machine, the integral of the product of two functions can be found. The operations involved consist, first, in plotting the curve $y = \psi(x)$, then in making the instrument, by a rather difficult attachment, yield a trace of the curve $y = \int_0^x \psi(x)dx$, then in plotting the curve $y = \phi(x)$: these two latter curves have to be wrapped round one or two cylinders. When the cylinders are caused to revolve, a pointer capable of moving parallel to the axis of y has to be kept on each curve, the motions of the two pointers being communicated to the disk and globe respectively of the integrator : the amount of the angular movement of the cylinder gives the integral.

In view of the very important part that the analysis of an arbitrary function into its harmonic constituents is destined to play in extracting law out of the immense mass of physical and chemical measurements that are being accumulated, it seemed to be worth while to look for a simpler method of obtaining $\int \phi(x)\psi(x)dx$ than the above. The following may be found to be such, and seems likely to be capable of more immediate application ; for the disk, globe, and cylinder integrator, despite its kinematical elegance, has not yet come into general use.

The following method is merely a mechanical realization of the operations which Fourier so carefully describes in his 'Analytical Theory of Heat,' art. 220, chap. iii. sect. vi., in order to give as concrete an idea as possible of the meaning of the coefficients in his expansion. " We see by this that the coefficients a, b, c, d, e, f which enter into the equation

$$\tfrac{1}{2}\pi\phi(x) = a \sin x + b \sin 2x + c \sin 3x + d \sin 4x + \&c.,$$

and which we found formerly by successive eliminations are the values of the definite integrals expressed by the general term $\int \sin ix\phi(x)dx$, i being the number of the term whose coefficient is required. This remark is important, because it shows how even entirely arbitrary functions may be developed in series of sines of multiple arcs. In fact, if the function $\phi(x)$ be represented by the variable ordinate of any curve

---

[*] Communicated by the Author.

whatever, whose abscissa extends from $x=0$ to $x=\pi$, and if in the same part of the axis the known trigonometrical curve whose ordinate is $y = \sin x$ be constructed, it is easy to represent the value of any coefficient. We must suppose that for each abscissa x to which corresponds one value of $\phi(x)$ and one value of $\sin x$, we multiply the latter value by the first, and at the same point of the axis raise an ordinate equal to the product $\phi(x) \sin x$. By this continuous operation a third curve is formed, whose ordinates are those of the trigonometrical curve reduced in proportion to the ordinates of the arbitrary curve which represents $\phi(x)$. This done, the area of the reduced curve taken from $x=0$ to $x=\pi$ gives the exact value of the coefficient of $\sin x$."

To take the more general case, let it be required to find $\int_{a_1}^{a_2} \phi(\theta)\psi(\theta)d\theta$. Plot the two curves whose polar equations are $r=\phi(\theta)$, $r=\psi(\theta)$, using the same pole and the same initial line for angular measurement in both cases. Let S_1 and S_2 be the points on the two curves corresponding to any value of θ (see figure); then

$$\psi(\theta)\phi(\theta) = OS_1 . OS_2.$$

Describe a circle of radius R passing through S_1 and S_2; through Q draw the tangent O T to this circle, then

$$OT^2 = OS_1 . OS_2.$$

Now if the arm OS_1S_2 is turned into any other position, cutting the curves in two fresh points S'_1 and S'_2, and if the circle of constant radius R is again brought into position so as to pass through these points, the new length of the tangent OT' is always such that $OT'^2 = OS'_1 . OS'_2$: therefore generally $OT^2 = \psi(\theta)\phi(\theta)$.

In OS_1S_2 mark off $OS_3 = OT$; then if, as OS_1S_2 is revolved from the initial to the final position, or from that given by $\theta=\alpha_1$ to that by $\theta=\alpha_2$, the motion of T is by any mechanical device communicated to S_3 unaltered, the locus of S_3 is a curve such that always $OS_3^2 = \phi(\theta)\psi(\theta)$;

$$\therefore \int_{a_1}^{a_2} \phi(\theta)\psi(\theta)d\theta = \int_{a_1}^{a_2} OS_3^2 \, d\theta$$
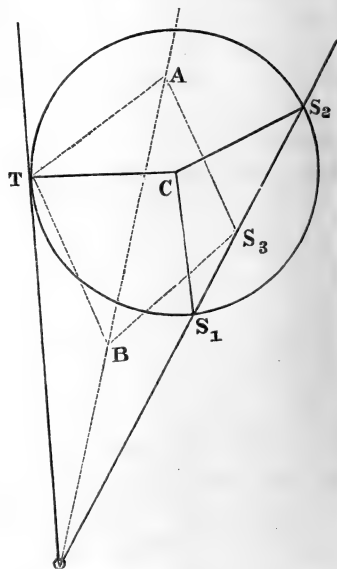
= twice the area of the figure enclosed by the third curve traced out by S_3, and by the lines $\theta = \alpha_1$, $\theta = \alpha_2$.

The arrangements for describing the third curve mechanically are obvious. An arm, OS_1S_2, capable of turning freely in the plane of the paper round an axis through O, bears two collars, S_1 and S_2, free to move along OS_1S_2; and to these, two equal arms, S_1C, S_2C, are freely jointed, being at the same time each free to turn in the plane of the paper round an axis through C ; the two collars bear pointers with which to follow the two curves. A second long arm, OT, can turn round the axis through O ; at T is a collar free to move along OT, and to it is rigidly attached an arm, CT, equal to CS_1 and CS_2, and always at right angles to OT : this arm bears the axis through C. Then as S_1 and S_2 are guided along the corresponding curves, the two arms OT and CT move in such a manner that T is always the point in which a circle of radius CS_1, CS_2, or CT is touched by OT; thus always $OT^2 = OS_1 . OS_2$.

As regards the transmission of the motion of T to a point S_3 on the axis OS_1S_2 different methods are possible, perhaps the simplest being that represented by the dotted lines in the figure. $ATBS_3$ is a rhombus with hinges at the four angular points ; the hinges at T and S_3 are attached to the collars there, while the hinges at A and B bear two collars free to move along an arm OBA, which in its turn is free to move round the axis through O, obviously always $OS_3 = OT$. A pencil attached to the collar S_3 traces the required curve.

All that is necessary, then, for finding the integral

$$\int_{\alpha_1}^{\alpha_2} \phi(\theta)\psi(\theta)d\theta$$

is to join the two ends of this curve by straight lines to O and take the area of the resulting figure by means of any planimeter.

But a very simple attachment to the above mechanism makes a planimeter of it. Suppose the area of any figure to be required. Fix the collar S_1 at a certain suitable distance b from O, so that when the arm OS_1S_2 moves, S_1 must describe a circle of known radius b. Guide S_3 along the outline of the figure, then S_2 moves always in such a way that

$$\int OS_3^2 d\theta = \int OS_1 . OS_2 d\theta = b \int OS_2 d\theta ;$$

but this last integral is the length of the path travelled by S_2. Thus all that is necessary is to attach at S_2 a wheel which will record the length of the path traversed by S_2.

The whole operation, then, of finding $\int_{\alpha_1}^{\alpha_2} \phi(\theta)\psi(\theta)d\theta$

resolves itself into the plotting of the two curves $r = \phi(\theta)$, $r = \psi(\theta)$, between the limits $\theta = \alpha_1$, $\theta = \alpha_2$, the fixing of the instrument so that its axis passes through O, the pole chosen in plotting the curves, the driving of the two pointers S_1 and S_2 along the two curves (which is easily done by one person) causing S_3 to trace a third curve between the same limits; then the clamping down of S_1, the forcing of S_3 to follow back its former track, and the reading of the revolutions of the wheel attached at S_2 during this last part of the performance. This reading gives the required value of the integral when the scales on which the two curves were drawn are taken into account. These scales must be chosen so that the maximum difference between OS_1 and OS_2 shall at least not be greater than the diameter of the circle whose radius is CS_1. In the above description, the word collar is used to mean any form of connection that allows with as little friction as possible one degree of relative freedom.

Melbourne, June 1, 1885.

XXII. *On the Sensitiveness of Selenium to Light, and the Development of a similar Property in Sulphur.* By SHEL-FORD BIDWELL, *M.A., LL.B.*[*]

THE remarkable property apparently possessed by crystalline selenium of having its electrical resistance varied by the action of light, a property which was first announced by Mr. Willoughby Smith in 1873, has been the subject of many investigations[†]. Of these the best known, and by far the most exhaustive, are the researches of Prof. W. G. Adams and Mr. R. E. Day, an account of which is published in the Phil. Trans. of 1877. As the result of numerous experiments, these gentlemen were led to form the opinion, that "the electrical conductivity of selenium is electrolytic"[‡]. The principal reasons given for this conclusion are:—(1) that the resistance of the selenium-bars used appeared to depend upon

[†] Willoughby Smith, Journ. Soc. Tel. Eng. ii. p. 31; Earl of Rosse, Phil. Mag. March 1874, p. 161; Sale, Proc. Roy. Soc. 1873, p. 283; Phil. Mag. March 1874; Werner Siemens, Phil. Mag. November 1875, p. 416; Draper and Moss, 'Chemical News,' xxxiii. p. 1; Adams and Day, Proc. Roy. Soc. 1876, p. 113; Phil. Trans. 1877, p. 313; C. W. Siemens, Proc. Roy. Inst. 1876, p. 68; Sabine, Phil. Mag. June 1878, p. 401; Graham Bell, 'Nature,' xxii. p. 500; Shelford Bidwell, Phil. Mag. April 1881, and January 1883; Fritts, 'Electrical Review,' March 7, 1885, p. 208.
[‡] Phil. Trans. vol. 167, p. 328; Proc. Roy. Soc. 1876, p. 115.

the electromotive force of the battery employed, being generally diminished as the battery-power was increased; (2) that the resistance of a bar AB was generally not the same for current in the direction AB as for a current in the direction BA; (3) that the passage of a battery-current was always followed, when the battery had been disconnected, by a secondary or polarization-current in the opposite direction, it being clearly proved that this secondary current was not due to any thermoelectric action, either in the selenium itself or in any other part of the circuit.

The authors do not, however, appear to have considered that the observed behaviour of selenium was to be explained by actual electrolysis, but rather that the molecular structure or crystalline condition of the substance was altered or modified by the action of a current of electricity in such a manner as to produce effects analogous to those which would have occurred if the selenium were an electrolyte and actually decomposed by the current. As to the possible influence of light, the following are their words *:—" Light, as we know, in the case of some bodies, tends to promote crystallization, and when it falls on the surface of such a stick of selenium, tends to promote crystallization in the exterior layers, and therefore to produce a flow of energy from within outwards, which, under certain circumstances, appears in the case of selenium to produce an electric current. The crystallization produced in selenium by light may also account for the diminution in the resistance of the selenium when a current from a battery is passing through it, for, in changing to the crystalline state, selenium becomes a better conductor of electricity."

Attention has lately been again directed to the subject of selenium, and its behaviour under the influence of light, by the publication, by Mr. C. E. Fritts of New York, of a new and extremely ingenious method of constructing selenium cells†. He melts a thin film of selenium upon " a plate of metal with which it will form a sort of chemical combination . . . . . During the process of melting and crystallizing, the selenium is compressed between the metal plate upon which it is melted and another plate of steel or other substance with which it will not combine. . . . . The non-adherent plate being removed after the cell has become cool, [he] then covers that surface with a transparent conductor of electricity, which may be a thin film of gold-leaf. . . . . The whole surface of

the selenium is therefore covered with a good electrical conductor, yet is practically bare to the light, which passes through the conductor to the selenium underneath." The sensitiveness to light of cells constructed in this manner seems to be far in excess of anything that has been previously obtained ; and the " photoelectric " currents which (like the selenium bars of Messrs. Adams and Day) they are capable of originating, are said to be strong enough to be actually useful in practical work.

It is impossible to read Mr. Fritts's paper without being impressed by the resemblance of some of the phenomena which he describes to those of electrolysis. The mere arrangement of the apparatus—two metallic plates with a third substance between them—is in itself strongly suggestive ; while the unequal resistance offered by the two surfaces, and the generation of an independent electromotive force, in conjunction with the polarization-effects above referred to*, make it hard to believe that the conduction of selenium (in the form used in experiments) is not truly and literally electrolytic.

The only considerable difficulty in the way of this hypothesis arises from the fact that selenium is not an electrolyte. Ever since its discovery in 1817, selenium has been regarded as an element, and very strong evidence indeed would be necessary to deprive it of its elementary character ; this is perhaps the reason why the electrolytic theory has not previously been proposed. But there is a possible way out of the difficulty, which was suggested to me by the first words in the above quotation from Mr. Fritts's paper. He spreads the selenium upon a plate of metal *with which it will form a chemical combination*. Now selenium will, I believe, combine more or less easily with all metals, forming selenides ; and in experiments upon the conductivity of selenium, it has been usual to submit the substance to prolonged heating in contact with metallic electrodes. This prolonged heating (generally followed by slow cooling) has hitherto been called " annealing ;" and the undoubted fact that it diminishes the specific resistance of the selenium and increases its sensitiveness to light, has been explained by supposing that the process is favourable to perfect crystallization.

I venture to suggest, as the true explanation of the effect, that heating is favourable to a chemical combination between the selenium and the metal forming the electrodes, that a selenide is thus formed which completely surrounds the elec-

---

* " The existence of polarization," says Clerk Maxwell, " may be regarded as conclusive evidence of electrolysis." ' Electricity,' vol. i. p. 363.

trodes, and is perhaps diffused to some extent throughout the mass of the selenium*; and that the apparently improved conductivity of the selenium, together with the electrolytic phenomena which it exhibits, are to be accounted for by the existence of this selenide.

I have sometimes been tempted to think it possible that the apparent conductivity of selenium may in fact be *entirely* due to the impurities which it contains, and that perfectly pure selenium would be as good an insulator when in the crystalline form as it is in the vitreous condition. Vitreous selenium might contain a large percentage of conducting particles without sensible increase of its conductivity, but that this would not be the case with crystalline selenium, is rendered more than probable by the results of some experiments which I have described in a former communication†. If a conducting powder, such as graphite, is mixed with melted sulphur, even in small proportions, the mixture when cold is found to conduct electricity; while if a very large proportion of the same powder is incorporated with melted shellac, the shellac when cold remains sensibly as perfect a nonconductor as if it were pure. The explanation which I have given of these facts, and in support of which a number of experiments are quoted, is as follows:—The first mixture does not consist of a uniform structureless mass of sulphur, having particles of carbon imbedded in and completely surrounded by it: it is in fact an aggregation of little crystals of sulphur with carbon packed between them like mortar between bricks. The conduction thus takes place entirely through the carbon particles, which may be considered as extending in a series of chains from end to end of the mass. In the case of the shellac mixture, though the proportion of carbon may be larger than in the sulphur experiments, the resistance is still sensibly infinite, because the structureless shellac penetrates between and completely surrounds the carbon particles. Just in the same manner, selenium, when in the vitreous condition, would completely surround any particles of conducting selenides which it might contain; while, when the selenium was crystallized, the conducting particles would arrange themselves in the form of a network, capable of conveying a current of electricity.

Selenium which is free from impurities appears not to be an article of commerce. An analysis of samples collected by Professor Graham Bell from different parts of the world

* The selenium is necessarily for some time in a liquid state,
† Phil. Mag. May 1882, p. 347.

disclosed the presence of the metals iron, lead, and arsenic*, all of which would form conducting selenides.   Nevertheless I thought it would be worth while to ascertain roughly the specific resistance of a piece of selenium which, since it has come into my possession, has never been in contact with metal. The selenium (which was supplied by Messrs. Hopkin and Williams) was melted in a mould built up of slips of glass, crystallized and "annealed" in the usual way ; but, contrary to the general practice, it was *not* fitted with metallic electrodes before annealing.   A plate of crystalline selenium was thus formed, having a thickness of about 2 millim. and a superficial area of 1 square centim.   The two opposite surfaces were rendered smooth and clean by rubbing them upon a flat board covered with fine glass-paper, and the plate was placed between two layers of thick tinfoil which were pressed into good contact with it by a weight of 500 grammes.   When this arrangement was connected in circuit with 6 Leclanché cells and a reflecting galvanometer, a deflection was produced indicating a current of about $\frac{1}{50}$ micro-ampere.   Assuming the electromotive force of the battery to have been 10 volts, the resistance of the plate would be 500 megohms; and therefore the resistance of a cubic centimetre of the selenium between opposite faces (*i. e.* its specific resistance) would be 2500 megohms.   From the dimensions and resistance of a good selenium cell with copper electrodes, which I have in my possession, I calculated that the specific resistance of the selenium contained in it was about ·9 megohm.   Thus, so far as the result of a single rough experiment can be trusted, it appears that the conductivity of selenium which has been annealed in contact with copper is nearly 3000 times greater than that of selenium which has undergone similar treatment without the presence of a metal. Whether selenium, when perfectly pure, is altogether a non-conductor, would be an interesting question for an expert chemist to determine †.   It is sufficient for the theory which I am at present advocating that its specific resistance should be very high.

By assuming the admixture with the selenium of metallic selenides, an explanation is afforded of the following facts :—

(1) The diminished resistance produced by annealing.

(2) The fact, first pointed out by Graham Bell, that the resistance of selenium appears to depend greatly upon the nature of the metals of which the electrodes are formed.   For obtaining low resistance he recommends the use of brass in

* Paper read before the National Academy of Sciences, April 21, 1881.
† On more mature consideration I am inclined to think that it is *not*.

preference to platinum, and expresses his belief that the chemical action between the brass and selenium contributes to the low resistance of his cells, " by forming an intimate bond of union between the selenium and brass." *

(3) The fact observed by Adams and Day that there is generally a " diminution of resistance in the selenium as the battery-power is increased." The same phenomenon occurs in the mixtures of sulphur and carbon before referred to. It points to the existence of imperfect contact between conducting particles, the conduction partaking of the nature of disruptive discharge, and is consistent with the supposition that particles of conducting selenide are imbedded in the selenium †.

(4) The apparent production by a current through a piece of selenium of a " *set* of the molecules which facilitates the subsequent passage of a current in the opposite, but obstructs one in the same direction "‡. This would be accounted for by the electrolytic deposition of selenium (from the selenide) upon the anode.

(5) The polarization-effects, which would also proceed from electrolysis.

(6) " A slight increase of temperature of a piece of annealed selenium is accompanied by a large increase of electrical resistance "§. This also occurs in the mixture of sulphur and carbon, and is explained by supposing that the heat-expansion of the medium draws apart the conducting particles contained in it, causing them to have fewer points of contact with each other, and thus increasing the resistance of the whole ‖. A more considerable rise of temperature so greatly diminishes the specific resistance of the selenide (and perhaps of the selenium) as to more than counterbalance this effect; and thus it happens (as I have shown in a former communication ¶) that selenium cells have a " temperature of maximum resistance," which is generally a few degrees above the average temperature of the air.

(7) The resistance of prepared selenium is generally greatly diminished by the action of time. Prof. Adams found that the average resistance of a number of pieces of selenium was

* Lecture to American Assoc. 1880. Reprinted in ' Nature,' vol. xxii. p. 500.
† See " On the Electrical Resistance of Carbon-contacts," Proc. R. S. Feb. 1, 1883 ; and " On Microphonic Contacts," Journ. Soc. Tel. Eng. April 12, 1883.
‡ Adams and Day, Proc. R. S. 1876, p. 114.
§ Adams and Day, Phil. Trans. 1877, p. 342. See also Phil. Mag. Jan. 1883, p. 31.
‖ Phil. Mag. May 1882, p. 351.
¶ Phil. Mag. April 1881.

reduced to less than one fortieth in the course of a year *.
During this period the selenium had been in contact with the
metallic electrodes; and it seems possible that a larger quan-
tity of selenide than was produced in the first instance by the
process of annealing was slowly formed.   This would espe-
cially occur at the "marked end," or anode, where there
would naturally be a quantity of free selenium.

In the above argument it has been assumed that selenium
will combine directly with any metal with which it is brought
into contact, the combination being facilitated by the appli-
cation of heat.   In the case of such metals as copper, brass,
and silver this is undoubtedly the fact.   Indeed, an attempt
to make a selenium cell with silver wires was attended with
failure in consequence of the complete destruction of the
metal after contact with the melted selenium for only two or
three minutes.   It is, however, questionable whether platinum
(which was the metal used by Adams and Day) is, in any
sensible degree, attacked by selenium either at the ordinary
temperature or at that reached in the process of annealing.
With sufficient heat the two substances will undoubtedly
unite; and I have found that the surface of platinum-foil upon
which melted selenium has been kept for an hour or two at a
temperature probably of about 250° C. acquires a bluish-grey
colour which may be due to selenide.   But whether any ap-
preciable quantity of selenide is formed in the ordinary pre-
paration of crystalline selenium is a question only to be settled
by the aid of refined chemical operations which I am incom-
petent to undertake, and in the meantime the suggested theory
is left without direct confirmation.

But certain indirect evidence in support of my views has
been forthcoming.   Selenium is an element which, in its
properties, closely resembles sulphur, and attempts have from
time to time been made, hitherto without success, to develope
in sulphur that peculiar sensitiveness to light which is such a
remarkable characteristic of selenium.   It occurred to me
that if this property of selenium were really due to the acci-
dental existence of metallic selenides, then the admixture
with sulphur of metallic sulphides might be expected to lead
to similar effects.   It is not possible to "anneal" a stick of
sulphur or a sulphur "cell" previously furnished with metallic
electrodes, because sulphur does not, like selenium, solidify
and crystallize at a higher temperature than that of its first
melting-point.   But if it is true that the virtue of annealing
really lies in the fact that a chemical union of the two elements
is promoted by the action of heat, it is clearly immaterial

* Phil. Trans. *loc. cit.* p. 348.

whether the substances are heated together before or after the formation of the cell. Sulphur containing sufficient metallic sulphide to render it a conductor of electricity might be used in the construction of a cell which might be expected to be sensitive to light without any preliminary annealing. This turned out to be actually the case.

Silver was the metal chosen for the experiments on account of the facility with which it combines with sulphur.

Cell No. 1.—Five parts of sublimed sulphur and one part of precipitated silver were heated together in a porcelain crucible for about two hours. The mixture was from time to time stirred with a glass rod and was finally allowed to settle, so that the bulk of the sulphide and any free silver which might remain fell to the bottom of the crucible. When the temperature was slightly above the melting-point the liquid sulphur, which was perfectly mobile, though black with minute suspended particles of sulphide, was poured off for use. Two wires of fine silver * were then coiled side by side around a strip of mica 50 millim. long and 27 millim. wide ; the wires were about 1 millim. apart, and care was taken that they did not touch each other at any point. Some of the melted sulphur was spread evenly over one surface of the mica, the two wires being thus connected with each other through half their entire length by a thin layer of the prepared sulphur. When cold, this cell was connected in circuit with a battery and a galvanometer. It was found to conduct electricity, but its resistance was very high, being probably between 20 and 30 megohms. With the object of partially bridging over the intervals between the wires, the sulphur was melted by laying the cell upon a hot plate, and a piece of very thin silver-foil, measuring 25 millim. by 10 millim., was laid upon its surface: this was probably entirely converted into sulphide before the cell was again cold. The cell was now found by a bridge-measurement to have a resistance of 900,000 ohms †. Once more it was connected with a Leclanché cell and a suitably shunted galvanometer; the deflection was noted, and a piece of magnesium wire was burnt at a short distance from the sulphur. The deflection was immediately more than doubled; and when the magnesium was extinguished, the spot of light at once returned to very nearly its original position. The effect was almost as great when a glass trough containing a saturated solution of alum was interposed between the sulphur and the burning magnesium ‡.

* Supplied by Messrs. Johnson and Matthey.
† This resistance was afterwards found to be very variable, and it was never the same with a direct and a reverse current.
‡ This cell was exhibited in action at the Meeting of the Physical Society on May 23rd, and at the Soirée of the Royal Society on June 10.

Now it is well known that the resistance of sulphide of silver is greatly diminished by heat *, and it was therefore important to ascertain whether the effect just described was due to light or to heat. To speak more accurately—Is it an effect of *radiation* or of *temperature* ? Exposure to radiation, whether visible or invisible, is of course always accompanied by a certain rise of temperature, and confusion has sometimes arisen, especially in discussing the properties of selenium, from failure to distinguish between the direct effects of radiation, and the indirect effects which are primarily due merely to a rise of temperature †. In the photographic processes it is radiation *per se* that produces the observed results: in the best known processes, the effective rays happen to be those which correspond to the most-refrangible part of the visible spectrum together with the invisible rays beyond it. But by more recently discovered methods the " obscure heat-rays," as they are sometimes called, have been made available for photographic purposes ‡; and these do not act by virtue of any rise of temperature which they may cause, but exert direct chemical action upon the sensitized plate. Again, if a thermo-pile is exposed to radiation, an electromotive force is generated. Here, however, the effect of radiation is indirect ; it acts only through the medium of the heat which it produces; and if an equal and similarly distributed amount of heat were communicated to the thermo-pile by any other means (as by conduction), exactly the same effect would follow. In an ordinary selenium cell radiation acts both directly and indirectly, tending to produce opposite effects. The direct effect of the radiation, whether it be visible or infra-red or ultra-violet, is a diminution of the resistance of the cell; at the same time the radiation slightly raises the temperature of the cell, and so indirectly tends to increase its resistance. If a selenium cell in circuit with a battery and a galvanometer is suddenly exposed, by withdrawing a screen, to the radiation of a black-hot poker, a momentary swing of the galvanometer-magnet will at first indicate a fall in the resistance; but this will be almost immediately followed by a rise which will increase up to a certain limit as the temperature of the cell becomes higher. The same kind of thing occurs when the cell is exposed to the infra-red or red portions of the spectrum; but in the latter case the temperature-effect merely diminishes, instead of overpowering, that directly due to radiation. If the bridge method is used for measuring

---

* Faraday, Exp. Res. §§ 432–439.
† See Moser, Proc. Phys. Soc. 1881, p. 348.
‡ Captain Abney is said to have obtained a photograph of a kettle of boiling water by means of the invisible radiations which it emitted.

the resistance, it may easily happen that the effect of gradually rising temperature escapes notice, a balance not being obtained until the temperature has become constant ; and thus, probably, is to be explained the fact that different observers have attributed the most powerful action upon selenium to different parts of the spectrum, ranging from infra-red to greenish yellow.

The resistance of the sulphur cell which has been described, unlike that of most selenium cells, was diminished by a rise of temperature *.   When in circuit with a Leclanché cell and a galvanometer, the effect of holding a nearly red-hot brass rod at a distance of 3 centim. from its surface, was a gradual fall of resistance, which in 15 seconds was indicated by 23 scale-divisions.   When the rod was removed, the spot of light slowly returned to its original position, occupying several seconds in doing so.   It is certain that the temperature of the sulphur must in this experiment have been much higher than when it was exposed to burning magnesium, with a solution of alum interposed, yet the effect was very much smaller; moreover, it was gradual instead of instantaneous.

Another experiment seems to prove conclusively that the resistance of the cell is diminished by the direct action of radiation, quite apart from any effect which may be produced by an incidental rise of temperature.   On a cloudy day the cell, with the alum trough before it, was placed at a distance of 16 feet from a small window, all the other windows in the room being darkened.   With the same battery and galvanometer as before, it was found that closing the window-shutter caused an instantaneous swing of the spot of light through 90 scale-divisions in the direction indicating increased resistance; and when the shutter was again opened, there was immediately an equal swing in the opposite direction.   A delicate thermopile of 54 pairs, connected with an astatic reflecting-galvanometer of low resistance, was then put in the place of the sulphur cell, and the alum trough placed before the open end of the conical reflector attached to it.   On opening the window-shutter, a deflection occurred indicating a current which was found by trial to be equal to that produced by the radiation of the human body at a distance of 10 ft. 6 in.   It is needless to say that such a minute change of temperature as this implies was without sensible effect upon the resistance of the sulphur cell.   There can then be no doubt whatever that the whole of the observed effect of the light upon the sulphur

---

* This was not so with all the cells subsequently made. See description of cell no. 3 below.

was due to the action of radiation as such, any change of resistance resulting from the incidental rise of temperature being quite inappreciable.

Cell No. 2.—This was constructed in a somewhat different manner. A piece of silver-foil was laid upon the surface of the mica before the two wires were wound round it, and instead of having prepared sulphur spread upon one face, the whole was immersed in *pure* melted sulphur for a few minutes, and then carefully drained. Before this treatment the silver wires were of course short-circuited by the foil, but the liquid sulphur penetrated between them, forming a film of sulphide; and when cold, the resistance of the cell was about 100,000 ohms. Though this cell turned out to be somewhat less sensitive than the other, it seemed likely that, on account of its comparatively low resistance, it might be successfully used for a photophonic experiment. It was therefore connected in circuit with a battery of ten Leclanché cells and a telephone, and exposed to a rapidly interrupted beam of light. The telephone at once gave out a musical note, which was nearly as loud as that produced by a good selenium cell under similar circumstances.

The behaviour of this cell under changes of temperature was the same as that of the other.

Cell No. 3.—A mixture, consisting of equal parts of sublimed sulphur and precipitated sulphide of silver, was melted and spread on one surface of a slip of mica, around which two silver wires had been wound as before. No foil was used in this case. The resistance of this cell was diminished by radiation, but increased in a very marked manner by rise of temperature. A paraffin lamp, at a distance of 18 inches, produced a steady diminution of the resistance. When the lamp was placed at a distance of 10 inches, the galvanometer-needle first moved in a direction indicating a further fall of resistance; but after a few seconds, when the temperature began to rise, it turned in the opposite direction. On moving the lamp 6 inches nearer, there was at once a large deflection in the direction of increased resistance, the temperature-effect completely predominating over that of radiation.

Cell No. 4.—A strip of silver-leaf was attached to a glass plate by means of gold size, and the middle part of it was exposed to the vapour of boiling sulphur until both surfaces were completely blackened. The resistance of this cell was high, but for a few days it was extraordinarily sensitive, a reflected beam of sunlight instantly effecting a diminution of 80 per cent. in its resistance. About a fortnight after it was made, its sensitiveness had greatly fallen off.

All these cells resemble selenium in giving polarization-currents after being detached from the battery.

Supposing it to be true, then, that it is not in the selenium or sulphur itself, but in certain metallic selenides or sulphides, that the sensitiveness to light is resident, does it become easier to explain the phenomenon, or, rather, to deprive it of the unique position which it has hitherto appeared to hold, and assign to it a place among a class of analogous effects?

I believe that, at all events in the case of the sulphur-silver cell, it is principally at the surface of the *electrodes* that the effects of radiation are to be looked for.

If a current of electricity is passed through a mass of sulphide of silver having silver electrodes, silver will be deposited upon the cathode and sulphur upon the anode. The accumulation of silver upon the cathode will clearly produce no appreciable effect upon the conductivity of the arrangement, and need not be considered. But sulphur has an enormously high resistance, and the deposition of a mere film of free sulphur upon the anode would be sufficient to stop the current altogether. The current is not in fact stopped, because the deposited sulphur at once combines with the silver of the anode, merely adding a new layer to the electrolyte. Thus the metal of the anode gradually combines with the sulphur of the electrolyte ; and the conductivity of the arrangement will depend to a great extent upon the facility with which this combination is effected, the quantity of electricity which can pass in a given time being limited by the quantity of sulphur which is capable of uniting with the electrode in the same time.

Sulphur combines with silver far more readily than with iron. If, therefore, my views are correct, we should expect a cell with an iron anode to offer a much greater resistance than one which had an anode of silver, the material of the cathode, so long as it was a good elementary conductor of electricity, being of comparatively little importance. To test this idea, a cell was made consisting of electrodes of iron and silver imbedded in a mixture of sulphide of silver and sulphur. The cell being connected with a battery and a galvanometer, the deflection was 115 divisions when the current passed from the silver to the iron through the electrolyte, and only 4 divisions when the direction of the current was from iron to silver*. The resistance was therefore nearly 30 times as great with an

* The resistance of the galvanometer was 3483 ohms, and it was shunted with a coil of 20 ohms. The resistance of the Leclanché cell was about 5 ohms.

iron anode as with a silver anode. It is clear that this was not the result of bad contact between the iron and the electrolyte (such as was supposed by Graham Bell in the analogous case of selenium to account for the high resistance of a cell with platinum electrodes as compared with one in which the electrodes were made of brass), because such an effect would be independent of the direction of the current. Rather it seems that the resistances of the two anodes afford data for measuring the relative facilities with which sulphur combines with silver and with iron.

Assuming it to be thus experimentally proved that the resistance of a sulphur-silver cell depends largely upon the readiness with which sulphur unites with the anode, it follows that any cause which would assist this union would at the same time diminish the resistance. Now it is well known that certain chemical combinations are accelerated by the action of radiation—the explosive union of chlorine with hydrogen under the influence of sunlight being a familiar example. The question then suggests itself, Does sulphur combine with silver more readily when exposed to radiation than it otherwise would? There is, I believe, direct evidence that it does.

A glass plate, covered with silver leaf, was placed, with the silvered side downwards, over a crucible of boiling sulphur. One half of the plate was covered with a piece of black cloth, and the arrangement was exposed to bright sunshine. In a short time the visible portion of the silver was darkened, owing to its partial conversion into sulphide; the cloth was then removed, and the silver beneath it was found to be scarcely discoloured. There was a distinct line of demarcation between the two halves. The experiment was repeated with the same result.

Since this effect might possibly have been due to other causes than the action of light (such as the unequal condensation of sulphur vapour upon the covered and uncovered portions of the plate), the experiment was made in another form. A piece of silver leaf attached to glass was brushed over with a solution of sulphur in bisulphide of carbon ; and in order to keep the temperature low and uniform, the silvered glass plate was immersed in a basin containing cold water, which was placed in the sunshine. A board was laid across the top of the basin so as to shade one half of the plate, the other half being exposed to the direct rays of the sun. In a quarter of an hour the exposed portion of the silver had acquired a dark brown colour, while that which had been protected was of a pale yellow tint, the outline of the shadow of the board being sharply defined. I think we have here the strongest evidence

that the combination of sulphur with silver is assisted by radiation.

But it is not perhaps necessary to assume that the effective action of light is confined entirely to the surface of one of the electrodes. If, as is commonly believed, electrolytic conduction involves a series of decompositions and recompositions throughout the electrolyte, any cause which assists either the separation or recomposition (or both) of the components of the electrolyte might be expected to increase its conductivity ; and it seems reasonable to suppose that the same influence which would assist the union of two substances when they have a tendency to unite would also be favourable to their separation when they have a tendency to separate. It is not impossible, therefore, that radiation, acting upon the surface of a thin layer of sulphide of silver through which an electric current is passing, might, by facilitating the molecular rearrangement of the atoms of sulphur and silver, exert a material influence upon the conductivity of the sulphide*.

So far as regards the explanation of the effect of light upon the resistance of selenium, I am aware that this paper contains little more than speculative suggestions, which are at present almost entirely unsupported by experimental evidence†. It is, however, noteworthy that these speculations led to the construction of a cell which, without containing a particle of selenium, behaved almost exactly as if it were composed of that substance. How far this may be considered to prove anything with regard to selenium I do not know ; but in any case the discovery of another substance possessing the same remarkable property seems in itself to be a matter of some interest.

XXIII. *On a New Law, analogous to those known under the names Law of Avogadro and Law of Dulong and Petit. By* J. A. Groshans‡.

[Concluded from p. 30.]

IT may be said that, as yet, the study of the causes which influence the value of x has to be commenced, and that all that pertains to this constant is still uncertain. Still I

* There are some experimental reasons, into which I am not at present prepared to enter, for believing that the admixture with the sulphide of a certain amount of free sulphur is necessary for the development of sensitiveness to radiation.

† It is especially desirable to ascertain experimentally whether the combination of selenium with the metals used as electrodes in selenium cells is assisted by light.

‡ Communicated by the Author. Translated by W. W. J. Nicol, M.A., D.Sc.

may be permitted to embody in the following pages the principal observations that I have been able to make on this subject ; and as in doing so I shall have frequently to refer to glycerine, it is perhaps as well to make a few remarks on its boiling-point.

There is but little agreement to be found among the figures given by various experimenters who have attempted to determine the boiling-point of this compound, $C_3 H_8 O_3$. The older experiments point to 9 as the value for x, the more recent to 9·5.

$$s\sqrt{9}=275 \cdot 1 \text{ and } s\sqrt{9 \cdot 5}=290 \cdot 1^*.$$

In this connection I may add that Wurtz's butylic glycol, $C_4 H_{10} O_2$, boils at 183°–184°, that of Kekulé at 201°–204° :

$$s\sqrt{8 \cdot 5}=182 \cdot 9, \quad s\sqrt{9}=196^{\circ} \cdot 2.$$

In the following table I have adopted 9 as the value of x for glycerine.

Glycerine exhibits a peculiar property with regard to x— it is this :—In glycerine, $C_3H_5(OH)_3$ one, two, or three of the hydrogens in hydroxyl groups may be replaced by ethyl, C_2H_5, to form ethylines. The original glycerine and its three derivatives form a species of homologous series the members of which have the common difference C_2H_4, and yet the increase of molecular weight is attended by a lowering of the boiling-point, exactly the opposite of what is observed in the case of other homologous series : this anomalous behaviour I attribute to the "*constancy of x*." In fact glycerine and its derivatives have all the same constant Tn/a, and consequently the same value of x—*i. e.* 9. The theoretical value of Tn/a, when $x=9$, is 83·41, as will be seen from the table. Other derivatives similar to the ethylic ones also possess the same constants.

Table XV.

Name of substance.	Formula.	a.	n.	S°, observed.	Tn/a.
Glycerine	$C_3 H_8 O_3$	92	14	277	83·69
Monoethyline	$C_5 H_{12} O_3$	120	20	227	83·33
Diethyline	$C_7 H_{16} O_3$	148	26	191	81·51
Triethyline	$C_9 H_{20} O_3$	176	32	185	83·28
Triallyline..............	$C_{12} H_{20} O_3$	212	35	232	83·37

* Mendelejeff gives 290° at 760 millim.—W. W. J. N.

Methyl glycerine, $CH(OH)_3$, is not known, nor is methyl erythrite (methylphycite), $C(OH)_4$. But there are two compounds which have the composition of the ethylines of these two unknown bodies, and a third, which is the allyline of the former:—

$$(1) \quad C_7 H_{16} O_3 = CH(OC_2H_5)_3,$$
$$(2) \quad C_9 H_{20} O_4 = C(OC_2H_5)_4,$$
$$(3) \quad C_{10}H_{16}O_3 = CH(OC_3H_5)_3.$$
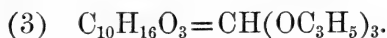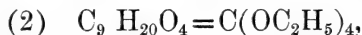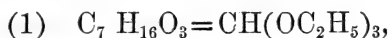
And these have all the same value of Tn/a, $x=7$. This property (the constancy of x) is to be met with in very many other cases. I ought, however, to observe that in reality this constancy of x is but a special case. When substitution-products are formed each has a particular value of x, which may be the same as that of the body from which it was formed, or may be greater or less than that by one or more units, according to circumstances.

In instances where the value of x for the original substance cannot be determined, it is frequently found that the products of substitution, or some of them, have the same x. This is the case with urea, $CO(NH_2)_2$. According to Table I., the value of B is 12. Table XVI. contains four substituted ureas; $x=16$ in three cases, but in the fourth $= 11$; or a difference of 5—a number which we shall find later on is a very frequent difference in the value of x for analogous bodies. In the following table I have, instead of the constant TB/a, inserted the value of x, $=1(27\cdot8)^2 \times (TB/a)^2$, which is the same thing, but in this instance more convenient. The boiling-points are the mean of those given in Fehling's dictionary.

TABLE XVI.

Name.	Formula.	A.	B.	S°, observed.	x, found.	x, calculated.
Urea	$CO(NH_2)_2$ ...	60	12			
Dimethyl urea ...	$CO(NHCH_3)_2$	88	18	269	15·90	16
Methylethyl urea.	$CO{}^{NHCH_3}_{NHC_2H_5}$ ...	102	21	267	15·99	16
Diethyl urea	$CO(NHC_2H_5)_2$	116	24	263	15·91	16
Tetramethyl urea.	$CO(N(CH_3)_2)_2$	116	24	176	11·16	11

In the last column of the table is given the theoretical value of x, which is simply the whole number nearest to the found

value. In Table XVII. the constancy of x is given in the case of the hydrazines, bodies resembling in formulæ urea; and the hypothetical first member, N_2H_4, differs from that in the ureas, CON_2H_4, by the group CO.

TABLE XVII.

Name.	Formula.	A.	B.	S°, observed.	x, found.	x, theory.
Hypothetical first member	$\left\{ \begin{array}{l} NH_2 \\ NH_2 \end{array} \right\}$ 32		10			
Phenyl hydrazine	$\left\{ \begin{array}{l} NHC_6H_5 \\ NH_2 \end{array} \right\}$ 108		20	233	11·36	11
Diethyl hydrazine ...	$\left\{ \begin{array}{l} NHC_2H_5 \\ NHC_2H_5 \end{array} \right\}$ 88		22	96·5	11·10	11
Phenylmethyl hydrazine...	$\left\{ \begin{array}{l} NHC_9H_5 \\ NHCH_3 \end{array} \right\}$ 123		23	223	11·13	11

Here, again, is the value of $x = 11$, as was the case in one of the bodies in the last table*.

Table XVIII. contains ethylene diamine, $C_2H_4N_2H_4$, and its substitution-products, along with an analogous compound,

TABLE XVIII.

Ethylene diamine and its substitution-products.

Formula.	a.	B.	S°, observed.	x, found.	x, calculated.
$N_2H_4(C_2H_4)$	60	16	117	13·99	14
$N_2H_2(C_2H_4)_2$	86	20	170	13·73	14
$N_2(C_2H_4)_2(C_2H_5)_2$	142	32	185	13·72	14
$N_2(C_2H_4)_3$	112	24	210	13·86	14
$N_2(C_2H_4)_3$	103	26	208	19·07	19

---

* We find in the aromatic series bodies metameric with those in Table XVII.; thus:—

Metamers of $C_6H_8N_2$.

Three phenylene diamines, with the constants x respectively = 12, 13, 14.

Metamers of $C_7H_{10}N_2$.

Three cresylene diamines, with x respectively 14, 13, and 14.

In ammonia, NH_3, $x = 9$; and thus we find that in the three series of bodies of which the three following are types there is a steady increase of x apparently without limits:—

$$\text{Ammonia, } NH_3, \quad \ldots \ldots \quad x = 9,$$
$$\tfrac{5}{}$$
$$\text{Ethylene diamine, } N_2C_2H_8, \quad . \quad x = 14,$$
$$\tfrac{5}{}$$
$$\text{Triethylene triamine, } N_3C_4H_{13}, \quad x = 19;$$

the difference NC_2H_5 therefore corresponds to $x = 5$, or in the atomic weight $= 43$, in density numbers $= 10$, numbers comparable with those observed in the case of the elements (see above).

It is also possible to use the property of *the constancy of x in substitution-products* to determine the value of some density-numbers, especially that of chlorine. It is found that, in general, x does not change when 1, 2, 3, or more atoms of chlorine are substituted for 1, 2, 3, or more atoms of hydrogen in a body of the formula $C_pH_qO_r$. Table XIX.

Table XIX.

Toluol and its Chlorine substitution-products.

Formula.	a.	B.	S°, observed.	T. B/a.
C_7H_8	92	15	108 N	62·1
C_7H_7Cl	126·5	18	164 L	62·18
$C_7H_6Cl_2$............	161	21	206 W	62·48
$C_7H_5Cl_3$............	195·5	24	237 L	62·61
$C_7H_4Cl_4$............	230	27	255 L	61·98

N = Noad; L = Limpricht; W = Wicke.

shows this clearly in the case of the four chlorine derivatives of toluol, C_7H_8; for when the density-number of chlorine is taken as 4, the value of the constant Tn/a is all through 62·2, and x is equal to 5. In the case of benzol, C_6H_6, $x = 4$, and so also for C_6H_5Cl, $C_6H_4Cl_2$, and $C_6H_3Cl_3$; while $x = 4·5$ for $C_6H_2Cl_4$ and C_6HCl_5. But $= 5$ for C_6Cl_6.

I have published, elsewhere [*], extended tables showing clearly this constancy of x in chlorine substitution-products.

---

[*] *Annalen*, Wiedemann, 1879, p. 134; J. A. Groshans, *Ein neues Gesetz*, Leipzig, Barth, 1882, p. 43; J. A. Groshans, *De la nature des Éléments*, Haarlem, héritiers Loosjes, 1875, p. 47.

It follows from this that numerous analogous compounds have the same value for x. In the following examples I have, for the sake of conciseness, omitted the numerical data, giving only the value of x deduced from the observed boiling-points :—

Examples of the Constancy of x.

(α) Methylic and Ethylic compounds, with Oxygen, Sulphur, Selenium, and Tellurium.

$(CH_3)_2$ O,	$x=3$.	$(C_2H_5)_2$ O,	$x=5$.
$(CH_3)_2$ S,	$x=3$.	$(C_2H_5)_2$ S,	$x=5$.
$(CH_3)_2$ S_2,	$x=3$.	$(C_2H_5)_2$ S_2,	$x=5$.
$(CH_3)_2$ Se,	$x=3$.	$(C_2H_5)_2$ Se,	$x=5$.
$(CH_3)_2$ Te,	$x=3$.	$(C_2H_5)_2$ Se_2	$x=5$.
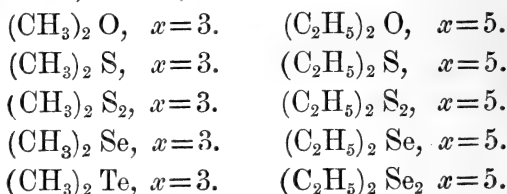
x in every case $=m$.

(β) Analogous compounds of Carbon and Silicon.

CCl_4,	$x=2$.		
$SiCl_4$,	$x=2$.	$(CH_3)_4$ C	$x=6$.
$CHCl_3$,	$x=2$.		
$SiHCl_3$,	$x=2$.	$(CH_3)_4$ Si,	$x=6$.
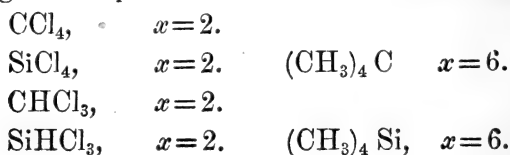
Here again $x=m$.

(γ) Analogous compounds of the members of the *triad*, Phosphorus, Arsenic, and Antimony.

$(CH_3)_3$ P,	$x=5$.	PO $(C_2H_5O)_3$,	$x=7$.
$(CH_3)_3$ As,	$x=5$.	AsO $(C_2H_5O)_3$,	$x=7$.
PO $(CH_3O)_3$,	$x=5$.	PI_3,	$x=7$.
AsO $(CH_3O)_3$	$x=5$.	SbI_3,	$x=7$.
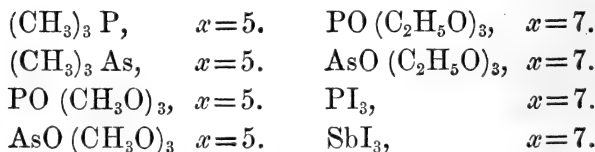
$x=7$, also for $HgCl_2$, $HgBr_2$, HgI_2, and Hg_2I_2.

On the Temperatures T $(273° + S°)$ *considered as proportional to the Molecular Volumes of Substances in the Gaseous State at the Boiling-point* S°.

We are accustomed to regard the absolute boiling-points as quantities expressing degrees of heat, and this no doubt they are ; but they are at the same time proportional to the molecular volumes of the vapours, analogous to those of the liquids at the boiling-point $(v_s = a/d_s)$. When the vapour-density D_s is expressed in terms of the volume of a gram of water at 4° C., the absolute boiling-point T (affected by a

constant coefficient) expresses the volume in cubic centimetres of the molecular weight in grams.

In explaining this I may be permitted to restate a few well-known facts.

Two grams of hydrogen at 760 millim., and at 0° C., occupy 22327 cubic centim.

a grams of any substance in the state of gas under the same conditions of temperature and pressure also occupy 22327 cubic centim., both by convention and in accordance with Avogadro's law.

This constant volume 22327 cubic centim. is multiplied at the boiling-point S° by the fraction T/273; and consequently the volume (molecular) of a substance in vapour at its boiling-point is

$$v_s = 22327 \, \mathrm{T}/273 = 81 \cdot 8 \, \mathrm{T} \text{ cubic centim.},$$

and the vapour-density is

$$\mathrm{D}_s = a/v_s = a/81 \cdot 8 \, \mathrm{T}.$$

As the coefficient 81·8 is the same for all bodies, it may be omitted if it be thought fit to do so.

Relation between the Gaseous Molecular volume V_s and the Liquid Molecular volume v_s.

When we take equal volumes (*e.g.* cubic centims.) of different liquids at S° and convert them into vapour by heating, we obtain a certain number of cubic centim. of vapour at 760 millim. and at S°; this number is for any substance whatever.

$$81 \cdot 8 \, \mathrm{T}/v_s \text{ (cubic centim.).}$$

In this connection I wish to draw attention to a special case which appears of particular interest : it is as follows :—

We find that in certain groups of analogous substances

$$81 \cdot 8 \, \mathrm{T}/v_s = \text{constant.}$$

This phenomenon is independent of the new law, and may be expressed as follows :—

$$\mathrm{V} \frac{273}{\mathrm{T}} = \text{constant} = v_r.$$

(The constant 81·8 is omitted here.)

I shall call the constant v_r the "reduced volume" of the substances in question.

When a cubic centimetre at $s°$ of the liquids (which have the same v_r) is volatilized, one obtains a definite volume of vapour which is the same for all these substances, and is

$$\text{vol. const.} = 22327/v_r \text{ cubic centim.}$$

Table **XX.** gives the value of v_r for some groups of these substances, and also the volumes (constant) of vapour.

TABLE XX.

Name.	Formula.	v_s.	S°, observed.	Authority.	v_r.	c. c. of vapour.
Toluol	C_7H_8	119·57	108	No.	85·7	260
Methyl benzoate ...	$C_8H_8O_2$	151·46	199	Pe.	87·7	255
Methyl salicylate ...	$C_8H_8O_3$	157·23	223	Kp.	86·5	258
Ether	$C_4H_{10}O$	105·97	35		93·9	238
Ethyl carbonate ...	$C_5H_{10}O_3$	140·56	126	Kp.	96·2	232
Ethyl propionate ...	$C_5H_{10}O_2$	128·08	100		93·7	238
Ethyl valerate	$C_7H_{14}O_2$	176·53	143	Kp.	115·8	193
Ethyl succinate......	$C_8H_{14}O_4$	209·71	217	Kp.	116·8	191

No=Noad; Pe=Peligot; Kp=Kopp.

It is clear that the phenomenon of the constancy of *vr* points to equality at the same time of the constants T*n*/*a* and $v_s n/a$; whence it follows that

$$\frac{v_s}{v'_s} = \frac{\mathrm{T}}{\mathrm{T'}}.$$

Here is another consequence of the above :—

Since it has been shown that the law of density numbers is applicable to the volumes of vapour T and T′ of compounds, it must also be applicable to the liquid volumes v_s and v'_s.

Application of the New Law to Volumes of Liquids at their Boiling-points.

The properties of the liquid volumes are different from those of the gaseous volumes. These last, when of isomeric bodies, can differ greatly; the former, on the other hand, are equal, or almost exactly so. But it seems to me a little premature to make any extended remarks on the subject of liquid volumes in general.

If d_s be the density of any liquid whatever at the boiling-point S°, the volume $v_s = \dfrac{a}{d_s}$; and in applying the law to these volumes we obtain the constants $v_s n/a$ analogous to T*n*/*a* (this constant $v_s n/a$ or $v_s B/a$ is the same as n/d_s or B/d_s). Instead of writing $v_s n/a$, I shall write k_s, which is more convenient. The following Table contains three groups, each of three members from Tables XIX. and XX. I have not been able to form larger groups, comprising 8–10 compounds, for the data relating to the volumes of liquids are too scanty.

TABLE XXI.

Names.	Formula.	*a.*	*n.*	Volume observed.	Observers.	k_s.
Ether	$C_4H_{10}O$	74	15	106·1	Kp.	21·51
Ethyl propionate ...	$C_5H_{10}O_2$	102	17	128·1	We.	21·34
Ethyl carbonate ...	$C_5H_{10}O_3$	118	18	138·8	Kp.	21·17
Toluol	C_7H_8	92	15	119·5	Lo.	19·49
Methyl benzoate ...	$C_8H_8O_2$	136	18	136·2	Kp.	19·89
Methyl salicylate ...	$C_8H_8O_3$	152	19	152·2	Kp.	19·63
Propylic oxide	$C_6H_{14}O$	102	21	151·6	Za.	31·21
Ethyl valerate	$C_7H_{14}O_2$	130	23	173·5	Kp.	30·70
Ethyl succinate......	$C_8H_{14}O_4$	174	26	209·0	Kp.	31·23

Kp. = Kopp; We. = Weger; Lo. = Longuinine; Za. = Zander.

Table XXII. contains several substitution-products resulting from the action of chlorine, bromine, and iodine on the alcohols and fatty acids.

TABLE XXII.

Name.	Formula.	*a.*	*n.*	v_s observed.	Observers.	k_s.
m = 2.						
Methyl alcohol	CH_4O	32	6	42·2	Kp.	7·91
Methyl bromide ...	CH_3Br	65	13	58·2	Pi.	7·96
Methyl iodide	CH_3I	142	18	68·3	Pi.	8·66
m = 3.						
Ethyl alcohol	C_2H_6O	46	9	62·0	Kp.	12·12
Ethyl chloride	C_2H_5Cl	64·5	11	71·2	Pi.	12·14
Ethyl bromide	C_2H_5Br	109	16	78·4	Pi.	11·51
Ethyl iodide	C_2H_5I	156	21	86·1	Pi.	11·59
m = 4.						
Propyl alcohol	C_3H_8O	60	12			
Normal	....	......	......	81·3	Za.	16·28
Iso-.................	....	......	......	82·7	Za.	16·59
Propyl chloride ...	C_3H_7Cl	78·5	14			
Normal	....	......	......	91·6	Za.	16·40
Iso-.................	....	......	......	93·8	Za.	16·78
Propyl bromide ...	C_3H_7Br	123	19			
Normal	....	......	......	97·4	Za.	15·03
Iso-.................	....	......	......	99·4	Za.	15·36
Propyl iodide	C_3H_7I	170	24			
Normal	....	......	......	107·2	Za.	15·13
Iso-.................	....	......	......	108·7	Za.	15·34
m = 6.						
Amyl alcohol.........	$C_5H_{12}O$	88	18	124·4	Kp.	25·45
Amyl chloride	$C_5H_{11}Cl$	106·5	20	137·0	Kp.	25·73
Amyl bromide	$C_5H_{11}Br$	151	25	149·2	Pi.	24·70
Amyl iodide	$C_5H_{11}I$	198	30	158·8	Kp.	24·06

Kp. = Kopp; Pi. = Pierre; Za. = Zander.

On the Variability of Physical Properties.

I have given the above name to the following phenomena:—

One frequently finds differences (according to Kopp reaching sometimes as much as 2 per cent.) in the density of the same substance at the same temperature. Similar differences are to be observed in the fusing- and boiling-points. Such differences present themselves when these physical properties have been determined by different persons or by the same observer at different times.

Space does not permit me to cite more than a very few instances.

I shall begin with crotonic acid, $C_4H_6O_2$; $a=86$, $n=12$. According to the law of density-numbers, and in consonance with analogy (which I need not further refer to), this acid should have the value of Tn/a corresponding to $x=5$, that is, the same constant as that of water.

There are three known isomers of this substance, which differ in chemical properties, with which I need not trouble my readers. One of these isomers, β, or isocrotonic or quartenylic acid, has the following physical properties ; it is a liquid, not solidifying even at $-15°$ C., and boiling at $171°-173°$; from $S° \sqrt{5}$ is calculated $172°·5$. There is thus complete concordance between the calculated and observed boiling-point.

With regard to the other isomers, their physical properties, as given in Fehling, are as follows :—

(1) a. acid—solid crotonic acid, tetracrylic acid : melting-point $71°-72°$, boiling-point $187°$ (corr.).

(2) Metacrylic acid : melting-point $+16°$, boiling-point $160°·5$.

We have seen above that the β or iso-acid has $x=5$. For its two isomers we find respectively $x=5·330$ and $x=4·734$; the mean value is $x=5·03$, which is essentially the same as $x=5$.

The particular fact that suggested to me the idea of the mean value for x in various isomers was as follows:—

"The liquid acid, which does not solidify even at $-15°$, is changed, by heating to $180°$ in a sealed tube, into the solid modification melting at $71°·5$ and boiling at $187°$" [*].

We may infer from this that the physical properties depend, among other things, on the treatment to which the compound has been subjected.

---

[*] Wurtz, *Dict. Suppl.* p. 551.

In this connection I shall take some other case from the paper by Thorpe on the molecular volumes of liquids, Chem. Soc. Journ. 1880.

Properties of the Compounds Br_2 and ICl.

The molecular weights of the above substances are respectively 160, 162·5, being very nearly equal, and both have $B = 18$. We would expect to find their densities (at the boiling-points) equal, but they differ by 0·1, or about 3·5 per cent. With regard to their densities at 0°C, δ_0, these are practically equal, notwithstanding the fact that their boiling-points differ by 42°. The following are the data relating to the above :—

	a.	B.	S°.	x.	d_0.	d_s.
Br_2	160	18	59·3	1·81	3·1883	2·9822
ICl	162·5	18	101·5	2·22	3·1822	2·8812

The values of x differ from the whole number 2 : the one is smaller, the other greater, the mean being $x = 2·01$. Where $x = 2$ for each body the respective boiling-points would be 76°·5 and 81°·9, which lie close together ; and the two densities d_s and $d'_{s'}$ would have been equal. I have calculated from the dilatations observed by Thorpe, what the densities would be at the calculated boiling-points : they are respectively 2·9244 and 2·9404.

It appears, then, that there exist in the case of these substances certain unknown causes which affect the boiling-points, raising the one 19°·4 and lowering the other 17°·5.

The existence of such an influence in very many cases will be strange to no one, for it has been suspected by many. It is the new Law, however, that points most clearly to it.

This also explains why the values of x, calculated from observed boiling-points, do not always present themselves as whole numbers, but are often affected by fractions, for instance :—

I have for valid reasons assumed that $x = 3$ in the case of the four following bodies (see above) :—

C_2H_6S . . $x = 3·28$. $\qquad$ $C_2H_6S_2$ . . $x = 3·12$.

C_2H_6Se . . $x = 3·05$. $\qquad$ C_2H_6Te . . $x = 3·27$.

The experiments of Thorpe (*loc. cit.*) furnish yet another example.

Properties of the Substances S_2Cl_2 *and* SO_2Cl_2.

These two bodies have the same molecular weight, the density-number is the same, $= 12$. The data are as follows:—

	a.	B.	S° obs.	*x* obs	d_0.	d_s.
S_2Cl_2	135	12	138·1	1·73	1·7094	1·4920
SO_2Cl_2	135	12	69·9	1·20	1·7081	1·5602

Mean . . $x = 1\cdot46$.

The boiling-points differ by $68°\cdot2$, but the almost perfect equality of the two densities d_0 points to the equality of x; and we may admit that the true mean value is $x = 1\cdot5$, which gives $110°\cdot1$ as the common boiling-point.

In the two sets of cases that we have examined above, it appears that the disturbing cause does not operate till above 0°C., the values of d_o are the same in each pair. But this is not always the case: for instance, in two isomers examined by Thorpe (*loc. cit.*),

	a.	B.	S° obs.	*x* obs.	d_0.	d_s.
$C_2H_4Cl_2$	99	14	83·5	3·28	1·2808	1·1563
$C_2H_4Cl_2$	99	14	59·9	2·86	1·2309	1·1092

Mean . . $x = 3\cdot07$. $s\sqrt{3} = 67\cdot5$.

Such a disturbing influence on the boiling-points and densities of liquids is of a nature to hinder the progress of the study of the physical properties of substances.

Compounds Liquid at the Ordinary Temperature.

The best method of applying the law of density-numbers to liquids is perhaps that based, as above, on the comparison of the volumes at the boiling-points ; but the data necessary for this comparison are but seldom available. When this is the case, we are still able in very many cases to verify the density-numbers simply by comparing together the values of d_o or d_t (*t* being the ordinary temperature $15° - 20°$C.) of analogous bodies, when the values of k_t will exhibit an agreement more or less complete.

In Table XXIII. an example is given of the above. The substances are arranged in the order of their boiling-points. By thus employing corresponding temperatures (slightly raised), it is possible to obtain satisfactory concordance in the values of k. When $t = 0$ the constants k_t arrange them-

<div align="center">Table XXIII.</div>

Formula.	S°obs.	B.	d_t.	$t°$.	k_t.
$C_6H_{15}As$......	140	29	1·151	16·7 (1)	25·20
$C_6H_{15}Sb$......	158·5	34	1·3244	15 (1)	25·67
$C_6H_{15}O_3As$...	167	32	1·224	0 (2)	26·14
$C_6H_{15}O_3P$ ...	191	27	1·075	0 (3)	25·12
$C_6H_{15}O_4P$ ...	215	28	1·086	0 (4)	25·78
$C_6H_{15}O_4As$...	236	33	1·3264	0 (2)	24·88

(1) Landolt; (2) Crafts; (3) Williamson; (4) de Clermont.

selves in the contrary order to that of the points of ebullition S°.

I have thought it interesting to compare with the above six compounds another, the formula of which resembles those of the bodies in the table: this is $((C_2H_5)_3Sn)_2$. Its properties are as follows:—

<div align="center">S°obs.   B. d_0. k_0.</div>

$C_{12}H_{30}Sn_2$ . . 237° (Ca.) 70 1·4115 (La.) 49·59.

Ca = Cahours; La = Ladenberg, who has found S = 267°. We have thus for

$$C_{12}H_{30}Sn_2 \quad . \quad . \quad k_0 = 2 \times 24·79,$$
$$C_6H_{15}O_4As \quad . \quad . \quad k_0 = 24·88,$$

A most complete agreement.

The value of k_t for liquids appears to depend on the value of p and q in the general formula $C_p H_q O_r$, for, as seen above, the atoms of O, S, and of metals, appear to exercise no influence. With regard to Cl, Br, I, they play the part of so many atoms of hydrogen: for instance, the three following metallic ethers should be considered to contain 16 atoms of hydrogen and not 15, for the constants k_t are a little higher than those of the compounds of As, P, &c., given above.

Formula.	S°obs.	d_t.	$t°$.	B.	K_t.
$C_6H_{15}ClSn$	209	1·428	8	39	27·32
$C_6H_{15}BrSn$	223	1·630	?	44	26·98
$C_6H_{15}ISn$	235	1·833	22	49	26·74

These are the experiments of Cahours.

I regret that space does not allow of my treating of corresponding temperatures and of the relative expansion of liquids, or of the application of this new Law to solutions.

XXIV. *Notices respecting New Books.*

Diary of a Magnetic Survey of a Portion of the Dominion of Canada, chiefly in the North-western Territories, executed in the years 1842–44. By Lieutenant LEFROY, *R.A., now* General Sir J. H. LEFROY, *C.B., K.C.M.G., F.R.S., &c.*

THE late Sir J. Herschel, in an article on "Terrestrial Magnetism," which appeared in the 'Quarterly Review,' June 1840, strongly advocated the carrying out of Magnetic Surveys of the Colonies. The late Gen. Sir E. Sabine, then Major R.E., in November 1840 addressed a letter to Sir J. Herschel, as Chairman of the Committee of Physics of the Royal Society, referring to the 'Quarterly Review' article, and containing proposals for a Magnetic Survey of the British Possessions in North America. The Committee laid this, and other letters on the subject, before the Council, with a strong recommendation that Government should be urged to have the proposed Survey executed. The Lords of the Treasury acceded to the proposal, and on July 20, 1842, Lieutenant, now General, Sir J. H. Lefroy, left England to take charge of the Observatory at Toronto, with the duty of carrying out the Magnetic Survey annexed.

This duty was completed by the close of 1844, and the general results only having been embodied in Sabine's memoir "Contributions to Terrestrial Magnetism" (Nos. 7 and 11, Phil. Trans. 1846, 1872), Sir J. H. Lefroy has been led by the renewed attention directed to the Distribution and Periodical Changes of the Earth's Magnetism, to present the observations of his Survey with fuller explanation and in a form more convenient for reference.

A Preface of pp. xxii gives the correspondence, out of which the Survey originated, as well as other particulars; concluding with some remarks on the subject of local anomalies in Magnetic Elements, reference being made, among other publications, to the recent Report of the U.S. Coast Survey for 1881.

Part I., pp. 58, is devoted to an account of the Instruments employed, and a general description of the observations made with them, followed by a discussion of the probable errors involved and other connected matters. To this succeeds the Diary of "a journey which was specially laid out for scientific work and almost excluded sport or excitement of any kind," containing the records of observations made from day to day between May 1843 and November 1844. Starting from Montreal the observers' route was up the Ottawa and down the French River to Lake Huron, along the N. shore of Lake Superior to Fort William, by way of Lake of the Woods, Lake Winnipeg, and Hill River to York Factory on Hudson's Bay, thence by Lake Athabasca to Fort Chipewyan (September 23), where the author "was warmly received by the late Mr. Colin Campbell, and resided with him until March 4, 1844. The arrival created a sensation in the small community, for it was twelve years since any traveller had arrived by canoe from the

south; and the self-importance of his *voyageurs*, who had thus happily completed a journey of 3600 miles, was conspicuous in their gala attire and gay *chansons* as the landing was approached." On the approach of spring the journey was resumed by way of Great Slave Lake to Fort Simpson on the Mackenzie River. At daybreak on March 28 the temperature sank as low as −41° F., and from the next day to May 25 Lieut. Lefroy remained at the Fort, awaiting the break-up of the ice, when the boats started for Fort Good Hope, lat. 66° 16′ N., long. 128° 31′ W. The return to Lake Athabasca (30th June) was by the same route, but from thence a détour was made up the Peace River to Fort Dunvegan, and by the Lesser Slave Lake, to Edmonton, from which point the River Saskatchewan was descended to Cumberland Harbour, reached on August 29. Useful Tables, Charts, and an Index complete the volume.

These records of field-work patiently and perseveringly carried out (a kind of work comparable in the labour involved with that of the Geodesic or Geological Surveyor in a new country) are not, of course, light reading, but are sufficiently interspersed with entries of difficulties encountered and overcome, risks run, physical and other features of the route observed, to impart much general interest to the narrative. The name of the author will now be inseparably associated with the few who have devoted themselves to build up the existing store of knowledge on the subject which has been secured for Science; while " Mount Lefroy," round the N.W. slopes of which the Canadian Pacific Railway will wind, when completed, will worthily perpetuate that name on the scene of those labours : *"Æternumque locus . . . nomen habebit."*

XXV. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 74.]

May 27, 1885.—Prof. T. G. Bonney, D.Sc., LL.D., F.R.S., President, in the Chair.

THE following communications were read :—

1. " On the so-called Diorite of Little Knott (Cumberland), with further Remarks on the Occurrence of Picrites in Wales." By Prof. T. G. Bonney, D.Sc., LL.D., F.R.S., Pres. G.S.

The Little Knott rock and its microscopic structure were briefly described by the late Mr. Clifton Ward, who named it a diorite, but called attention to its abnormal character. The author gave some additional particulars, and showed that although the rock varies in different parts of the same outcrop, and is not one of the most typical representatives of the picrite group, its relations on the whole are with this rather than with the true diorites. He also called attention to the extraordinary number of boulders which have been furnished by this comparatively small outcrop, and discussed the relation of their distribution to the former extension and effects

of ice in the Lake District. He briefly noticed the occurrence of additional boulders of picrite in Anglesey, and described specimens from two localities (Caemawr and Pengorphwysfa) where a similar rock has been discovered *in situ* by Professor Hughes. Hence it is probable that the Anglesey boulders are derived from localities in that island, and not from Cumberland. From a re-examination of specimens collected by the late Professor Sedgwick and Mr. Tawney, preserved in the Woodwardian Museum at Cambridge, the author showed that the rock must occur *in situ* in two localities in the Lleyn peninsula, in the neighbourhood of Clynnog and of Aberdaron. Lastly, he described a very remarkable picrite boulder, discovered by Dr. Hicks, which rests on " Dimetian " rock at Porthlisky near St. Davids.

2. " Sketches of South-African Geology.—No. 2. A Sketch of the Gold-Fields of the Transvaal, South Africa." By W. H. Penning, Esq., F.G.S.

The Gold-Fields of the Transvaal have been defined as covering nearly all the eastern and northern districts of the State, though but a small portion of the area is productive. In this paper the author described only the Lydenburg and De Kaap gold-fields, leaving those of Pretoria and Marabastadt for a future communication. The auriferous region is known to extend 350 miles to the northward beyond the Limpopo river, so that the gold-bearing rocks are found throughout at least $7\frac{1}{2}$ degrees of latitude and 3 of longitude.

The area of the two gold-fields mentioned, comprising together about 3000 square miles, was defined; and the Author, after noticing some old gold-workings, proceeded to give an account of the physical features of the country. He especially called attention to the circumstance that most of the rivers rise to the west of the highest range, and flow eastward through it.

The oldest gold-bearing rocks consist of unfossiliferous schists, shales, cherts, and quartzites, classed by the author as Silurian. Amongst these a great mass of coarse granitic rock is intruded, consisting of quartz and felspar, with but little, if any, mica. This granite, in the De Kaap valley, forms an ellipse 17 miles long by 10 broad, with a narrow northerly prolongation. Both the granite and the stratified rock are traversed by intrusive dykes, chiefly of diorite.

These beds have been much disturbed, and then cut down, probably by marine denudation, to a level plain 1700 or 1800 feet above the sea. Upon them rest unconformably a great sequence of conglomerates, sandstones, and shales, the " Megaliesberg beds " of a former paper, but now provisionally classed as Devonian. These rocks also are traversed by dykes of diorite and other kinds of trap. The " High Veldt beds " overlie the " Devonian " with some unconformity.

Several sections and observations illustrative of these facts were described, and details were given of the different gold-mines in each of the great systems noticed, and also in alluvial deposits. It was

shown that much gold was derived originally from veins in the older or Silurian rocks, and that some of that met with in the newer system occurred in conglomerates or other detrital beds. But there are also gold-bearing quartz-veins intersecting the latter.

3. "On some Erratics in the Boulder-clay of Cheshire &c., and the Conditions of Climate they denote." By Charles Ricketts, M.D., F.G.S.

The Author stated that the glacial phenomena of the valley of the Mersey indicate that the country has been entirely covered with ice and snow, resulting solely from the snowfall on its water-slopes and those of the tributary valleys. The glacial striæ coincide in direction with that of the respective valleys, or are in direct connection with the contour of the ground. The bottoms of the valleys are usually filled to some extent with irregularly stratified sands and gravels, containing erratic pebbles from which all striæ have been removed, probably by currents of water holding sand in suspension. Above these there is a boulder-clay containing a larger proportion of sand and gravel than the boulder-clay proper. The flanks of the valleys are covered with unstratified sand or fragments of sandstone derived from the Trias, probably left by glaciers as submarine moraines. The whole is overlain by the true boulder-clay, an unstratified reddish-brown clay containing erratics derived from different and distant localities. This clay originated in the grinding-action of the glaciers upon the neighbouring rocks, and was carried out in the form of mud by subglacial streams of water. The contained pebbles, many of which are smoothed, flattened, scratched, and striated, were carried by and dropped from icebergs and floating ice ; they are so abundant as to indicate that the bay of Liverpool was densely packed with ice.

The Author noticed the occurrence in these beds of masses of contemporaneous sands, gravels, &c. caused by changes in the extension of the glaciers, and described a large series of erratics derived from granitic, volcanic, Silurian, Carboniferous, and other rocks covered with striæ and other glacial markings, and also affording evidence of subsequent exposure to weathering before they were floated away and dropped into the clay. In connection with this weathering of the boulders, the Author remarked that in the case of the granitic and volcanic rocks the process differed greatly in degree, extending in some granites to the separation of each individual grain throughout the whole mass, and he called attention to the occurrence in Ireland of fragments of disintegrated granite and trap imbedded in moraines, eskers, and Boulder-clay, and to that of Wastdale-Crag granite similarly decomposed in the moraine in the neighbourhood of Shap, where also rocks of volcanic origin have become weathered in the same way as some in the Boulder-clay of Cheshire. Fragments of limestone also show traces of erosion, while others have been split into two or more pieces since their glaciation, phenomena also observed in moraine-accumulations in limestone-districts. Similar phenomena occur in the case of slaty and other

stratified rocks. Some limestone pebbles have been perforated by Mollusca and other marine animals.

The inference drawn by the Author from the facts recorded in his paper is that these weathered boulders once formed portions of moraines on land from which, for a time, the glaciers had receded, and that, after a succession of seasons sufficient to disintegrate these blocks more or less, an increased snowfall caused such an extension of the glaciers that the blocks were carried down to the sea and conveyed away in icebergs and by floating ice to the spots where they are now imbedded. As they occur at different horizons there must have been a repetition of the advance and retreat of the glaciers such as now occurs in Greenland.

June 10.—Prof. T. G. Bonney, D.Sc., LL.D., F.R.S., President, in the Chair.

The following communications were read :—

1. " Note on the Sternal Apparatus in *Iguanodon*." By J. W. Hulke, Esq., F.R.S., V.P.G.S.

2. " The Lower Palæozoic Rocks of the Neighbourhood of Haverfordwest." By J. E. Marr, Esq., M.A., F.G.S., and T. Roberts, Esq., B.A., F.G.S.

The authors in this communication described the sequence of the Lower Palæozoic rocks lying to the north of Haverfordwest and Narberth. Their work is founded on that published by the Geological Surveyors in their maps, sections, and memoirs.

To the north of the ridge of rock running eastward from Rock Castle, claimed as Archæan by Dr. Hicks, they have discovered Lingula Flags, with *Olenus spinulosus*, Wahl, and *Agnostus pisiformis*, Linn. These beds are seen underlain by conglomerate, resting upon older rocks, near Trefgarn Bridge.

South of Dr. Hicks's Archæan ridge, a great fault brings beds of Bala age in juxtaposition with the rocks of the ridge ; hence, in the tract described, no rocks of Tremadoc and true Arenig age have been met with. In the area south of the ridge the rocks are thrown into a complex synclinal, with a complex anticlinal to the south-east, near the town of Narberth.

The succession which the authors attempted to establish in this area is as follows (in ascending sequence) :—

    i. *Didymograptus* shales, with *Murchisoni*-form Graptolites.

    ii. Llandeilo limestone, with *Asaphus tyrannus*, Murch. &c.

    iii. *Dicranograptus* shales, with *Dicranograptus, Climacograptus bicornis, Diplograptus foliaceus*, &c., having a zone at the summit marked by the abundance of *Orthis argentea*, His.

    iv. Robeston Wathen Limestone, with many corals and Brachiopods, and few Trilobites.

    v. *Trinucleus-seticornis* beds, characterized by abundance of *Trinucleus seticornis*, His., and its variety *T. Bucklandi*. These are subdivided into three stages, viz. :—(*a*) Sholeshook limestone, with Cystideans and an abundant Trilobite fauna, including *Agnostus*

trinodus, Salt, *Trinucleus seticornis,* His., *Stygina latifrons,* Portl., *Phillipsia parabola,* Barr., *Cheirurus parvus,* Salt., *Encrinurus sexcostatus,* Salt., *Phacops Brongniarti,* Portl., &c.

(*b*) Redhill beds, blue-grey shales, generally poor in fossils, but containing here and there a fair abundance, especially of *Phacops Brongniarti,* Portl., and *Trinucleus Bucklandi,* Barr., and many Lamellibranchs and Gasteropods.

(*c*) Slade beds, consisting of gritty green shales with calcareous bands crowded with fossils. *Glauconome disticha, Phyllopora Hisingeri,* McCoy, *Phacops Brongniarti,* Portl., *Trinucleus seticornis,* His., *Calymene trinucleina,* Linn., *Orthis testudinaria,* Dalm., are abundant. *Climacograptus,* sp., also occurs.

vi. Conglomerate, containing many quartz pebbles, succeeds the beds of the Slade stage in many localities, and does not seem to mark a great discordance, as the authors have nowhere found it resting on lower beds.

vii. Lower Llandovery beds. Green gritty shales, with grit and very fossiliferous calcareous bands, characterized especially by *Nidulites favus, Petraia subduplicata,* var. *crenulata, Stricklandinia lirata,* &c., and containing *Phacops elegans,* Bœck and Sars, *Phacops mucronatus,* Ang., and *Deiphon Forbesi,* Barr.

The authors attempted a correlation of the Haverfordwest rocks with those of other areas :—

Conglomerate and grit of Trefgarn	= Harlech ?
Lingula Flags of Trefgarn &c.	= Dolgelly beds.
Didymograptus shales	= Llanvirn.
Llandeilo Limestone	= Lower Bala.
Dicranograptus shales	= Lower and Middle Bala.
Robeston Wathen Limestone	= Bala Limestone.
Trinucleus-seticornis beds	= Upper Bala.
Conglomerate ⎫ Fossiliferous Lower Llandovery beds ⎭	= Lower May Hill.

In conclusion the authors notice two points which require further elucidation. The first is the separation of the Robeston Wathen and Sholeshook limestone. This is made on palæontological and lithological grounds, as the whole thickness of the two limestones had nowhere been met with in the same section. The second is the relationship of the conglomerate to the fossiliferous Lower Llandovery beds. In the only place where the two appear in juxtaposition the conglomerate series appears to underlie the fossiliferous Llandovery beds ; this the authors explained by a faulted overfold. These difficulties do not, however, prevent the authors from hoping that the sequence they have established will be of use in assisting to determine the character of the very remarkable folds by which the district has been affected.

3. "On certain Fossiliferous Nodules and Fragments of Hæmatite (sometimes Magnetite) from the (so-called) Permian Breccias of Leicestershire and South Derbyshire." By W. S. Gresley, Esq., F.G.S.

In this paper the author described certain pebbles of hæmatite

and magnetite which occur in the so-called Permian breccias on the
western margin of the Ashby-de-la-Zouch Coalfield. These pebbles,
which are largely collected for sale and used as " burnishers," vary
in size from a diameter of $\frac{1}{10}$ inch to the size of a man's fist. They
present many varieties of form, have sometimes an agate-like struc-
ture, and occasionally exhibit well-marked magnetic polarity.
Sometimes they show grooving and striation resembling those pro-
duced by ice-action, while at other times they seem to have been
crushed and recemented. Many of these pebbles contain fossils of
various kinds, chiefly plant- and insect-remains, but with a few of
Annelids, Mollusca and Fish. All the fossils are of Carboniferous
age.

From the consideration of all the facts detailed in the paper, the
author concluded that these nodules were originally composed of
clay ironstone, and that they were derived from Carboniferous strata.
He considered that the pseudomorphic action by which they have
acquired their present composition must have taken place *in situ*
since their inclusion in the breccia.

June 24.—Prof. T. G. Bonney, D.Sc., F.R.S., President,
in the Chair.

The following communications were read :—

1. " Supplementary Notes on the Deep Boring at Richmond,
Surrey." By Prof. John W. Judd, F.R.S., Sec.G.S., and Collett
Homersham, Esq., F.G.S.

Since the author's former communication to the Society on the
subject, this boring, in spite of the strenuous efforts made by the
Richmond Vestry and the contractors, Messrs. Docwra and Co., has
had to be abandoned, after reaching a total depth of 1447 feet from
the surface. This depth is 145 feet greater than that of any other
well in the London Basin, and, reckoning from Ordnance Datum,
reaches a lower level by 312 feet than any other well in the district.

Before the termination of the work temperature-observations
were obtained, which, generally, confirm those previously arrived at.

The strata in which the boring terminated consisted of the red
and variegated sandstones and marls previously described, which
were proved to the depth of 208 feet. Although it was demon-
strated that these beds have a dip of about 30°, complicated in
places by much false-bedding, no conclusive evidence could be
obtained concerning their geological age. They may be referred
either to some part of the Poikilitic series, or to the Carboniferous
(for similar strata have been found intercalated in the Carboniferous
series at Gayton, near Northampton), or they may be regarded as
of Old Red Sandstone age.

Some interesting additional observations have been made since
the reading of the former paper, on the Cretaceous rocks passed
through in this well. Mr. W. Hill, F.G.S., of Hitchin, has found
the exact analogue of the curious conglomerated chalk met with at
a depth of 704 feet at Richmond. His observations entirely confirm

the conclusion that we have at this depth the "Melbourne Rock" with the zone of *Belemnites plenus* in a *remanié* condition at its base. Some new facts concerning the state of preservation of the fossils in the Chalk Marl are also recorded.

With respect to the conclusions arrived at by the author concerning the distribution of the Jurassic rocks on the south side of the London Basin, an important piece of confirmatory evidence has been supplied by a deep boring made at the Dockyard-Extension Works at Chatham. This section, for the details of which the authors are indebted to the officers of the Geological Survey, shows that under the Chalk and Gault, with normal characters and thickness, there lie 41 feet of sandy strata of Neocomian age, and that these are directly underlain by blue clays of Middle Oxfordian age, as is proved by the numerous fossils which they have yielded. We have now, therefore, direct evidence of the existence and position of strata of Lower, Middle, and Upper Oolite age, respectively, beneath the Cretaceous rocks of the south-east of England.

2. "On the Igneous and Associated Rocks of the Breidden Hills in East Montgomeryshire and West Shropshire." By W. W. Watts, Esq., F.G.S.

The author, in this paper, described the succession of rocks in the small tract near the Breidden Hills situated between Welshpool and Shrewsbury. The Cambrian rocks are:—

(1) Criggion Shales, dark and barren, much penetrated by intrusive diabases and about 2700 feet thick.

(2) Andesitic lavas and ashes, followed by conglomerates of the same materials.

(3) Ashy grits and shales containing *Climacograpsus antiquus?*, *C. bicornis?*, *C. Scharenbergi*, *Cryptograpsus tricornis*, *Diplograpsus foliaceus*, *Leptograpsus flaccidus?*, *Beyrichia complicata*, *Trinucleus concentricus*, *Orthis testudinaria*, *Bellerophon bilobatus*. The rocks are thus of Bala age, the fossils indicating that the ashy grits and shales are on the horizon of the top of the Glenkiln or bottom of the Hartfell series.

These are followed by Silurian strata.

(1) *Pentamerus*-beds. Soft sandstones and mudstones yielding *Pentamerus globosus?*, *P. oblongus*, *P. undatus*, *Leptæna transversalis*, *Strophomena rhomboidalis*, *Petraia subduplicata*.

(2) Purple shales, unfossiliferous.

(3) Lower Wenlock Shale, with *Monograptus vomerinus?*, *Cryptograpsus*, sp., *M. priodon*, var. *Flemingi*. These graduate into:—

(4) Upper Wenlock Shale, with *M. priodon*, *M. vomerinus?*, *M. basilicus*, *M. Nilssoni*, *M. Rœmeri*.

(5) Lower Ludlow Shale. *M. colonus*, *M. Nilssoni*, *M. Salweyi*, *M. lintwardenensis*.

The paper concluded with microscopical descriptions of the igneous rocks, of which there are two sets:—

(1) An older set interbedded with the Cambrian and consisting of andesites bearing a large percentage of a mineral allied to enstatite,

together with augite and a small quantity of hornblende and mica. These are chiefly lavas, but some few are perhaps intrusive rocks and dykes.

(2) Intrusive rocks of a diabase type, generally, however, containing a variety of enstatite identical with that in the andesites. These are intrusive in the Cambrian rocks, and from their relations appear to be most probably of Post-Silurian age.

3. "Note on the Zoological Position of the Genus *Microchœrus*, Wood, and its apparent Identity with *Hyopsodus*, Leidy." By R. Lydekker, Esq., B.A., F.G.S.

4. "Observations on some imperfectly known Madreporaria from the Cretaceous formation of England." By R. F. Tomes, Esq., F.G.S.

5. "Correlations of the Curiosity-Shop Beds, Canterbury, New Zealand." By Capt. F. W. Hutton, F.G.S.

The "Curiosity Shop" is a locality on the River Rakaia in the Canterbury Plains, and has been thus named on account of the numerous fossils found in some calcareous sandstones cut through by the river. The section exposed consists of

1. River-gravels.
2. Loose grey quartz sands.
3. Soft calcareous sandstone with glauconite, passing downwards into tufaceous clay.
4. Calcareous sandstone without glauconite.
5. Loose grey or yellowish brown sands.

By Mr. McKay, of the Geological Survey, No. 2 had been referred to the Pareora series (Miocene?), No. 3 to the Upper Eocene series, and Nos. 4 and 5 to the Cretaceo-Tertiary series. The author, who was inclined to class all these beds in a single series, pointed out that the only difference between the fossils found in Nos. 3 and 4, the most important fossiliferous beds, consisted in the presence of a greater number of forms in No. 3, all found in No. 4 being identical with those in the overlying bed. He then gave a complete list of the species of Vertebrata, Mollusca, Brachiopoda, Echinodermata, Bryozoa, and Cœlenterata, from the locality, 48 in all, and compared them with those from the Weka-pass stone, 26 in number, and the Ototara fossils from Oamaru, to show that a large proportion were identical. He gave reasons for not agreeing with the views of Dr. Hestor and Mr. McKay, who held that unconformity exists between the beds referred by them at the Curiosity Shop, in the Weka-pass district, and north of Otago, to the Upper Eocene and Cretaceo-Tertiary series respectively, and showed both from palæontological and stratigraphical data that all these rocks must be included in one system, the Oamaru system of Dr. von Haast and himself.

6. "On the Fossil Flora of Sagor in Carniola." By Constantin, Baron von Ettingshausen, F.C.G.S.

XXVI. *Intelligence and Miscellaneous Articles.*

ON HYGROMETRY. BY M. JAMIN.

M. MASCART publishes every year, in the *Annales du Bureau météorologique de France,* observations made in nearly one hundred stations all over France, and the same is the case in all European States. I have taken from them the pressure of the air at the base and on the summit of the Puy de Dôme, and I now desire to make a general remark on hygrometry.

On looking at the tables of *relative moisture,* it is surprising to see them so uniform. The means are almost the same in each moment and at all stations. Thus we find at Clermont Ferrand, at midday in the year 1880,

February.	June.	August.	September.	October.
593	599	570	569	622

It is, however, clear that there are great differences in the hygrometric conditions of the months of February and August, and that if these are not brought out in the tables it is, probably, that the system adopted in reducing the observations is erroneous.

This system consists in expressing the ratio $\frac{f}{F}$ of the elastic force observed f to the maximum force F, which air would have at the same temperature if the air were saturated; this is what is called the *relative moisture.* But for any given air of constant composition the quotient $\frac{f}{F}$ varies: 1st, with the proportion of vapour; 2nd, with the height and the barometric pressure, since f is proportional to this pressure; 3rd, and more particularly, with the temperature which changes the value of F; it is then a function of three independent variables; and we may hope that it brings out the variations in the quantity of vapour. We must for this eliminate the disturbing influences of pressure, of height, and of temperature, but that can easily be done.

When chemists analyze air, they determine the quantities of oxygen, nitrogen, and carbonic acid; to complete the analysis, it would be logical to add the proportion of aqueous vapour. As this vapour is a gas subject to the same laws of compression and expansion as other gases, there is no reason to measure it otherwise.

Let f be the tension of vapour, H the total pressure of the atmosphere, H$-f$ that of the dry air, we have

$$\text{Weight of vapour P} = \frac{v(1\cdot293)(0\cdot622)f}{(1+at)760}.$$

$$\text{Weight of dry air P}' = \frac{v(1\cdot293)(\text{H}-f)}{(1+at)760}.$$

$$\frac{\text{P}}{\text{P}'} = 0\cdot622\frac{f}{\text{H}-f}.$$

$\dfrac{P}{P'}$ is accordingly the ratio of the weight of vapour to that of dry air ; it is independent of pressure and temperature, for f and $H-f$ follow the same laws ; it expresses the *hygrometric richness* in weight, and $\dfrac{f}{H-f}$ measures its volume.

It may be remarked that the observations do not directly give the ratio ordinarily used, $\dfrac{f}{F}$. In fact, the condensing hygrometer measures f, which is a function of the pressure and therefore of the height ; the psychrometer determines $\dfrac{F'-f}{H}$; in order to pass from the measurement made to the function $\dfrac{f}{F}$, a calculation is made which serves no further purpose. By introducing the denominator F', we just introduce into the tables disturbances arising from the temperature which mask the influence of the vapour and complicate the result. It is no more difficult to calculate $\dfrac{f}{H-f}$ and keep the result, than to calculate and retain $\dfrac{f}{F}$; this would be replacing a complicated function, from which nothing can be deduced by an exact gravimetrical or volumetrical measurement of the hygrometric composition of the air.

I propose therefore to suppress the *relative moisture* $\dfrac{f}{F}$ in meteorological tables, and to replace it by the *hygrometric richness* $\dfrac{f}{H-f}$. In order to justify this substitution, I may show the effect by an example. I take the determinations made by M. Alluard at Clermont Ferrand in 1880, and published in the *Annales Météorologiques*. No very appreciable differences are seen in the different months ; the numbers decrease from the morning until 3 P.M., which shows the influence of temperature as by M. Angot. Nothing in it indicates change of moisture.

Clermont.—*Relative Moisture.*

	6.	9.	12.	3.	6.	9.
January	85·3	89·6	79·5	79·5	89·6	90·3
February	80·4	71·6	59·2	54·7	74·3	77·7
March	83·9	59·8	68·3	39·0	52·6	69·5
April	81·9	71·6	63·7	61·5	71·5	76·6
May	75·6	58·7	49·3	49·3	54·7	70·8
June	82·5	64·4	58·9	58·1	65·2	81·2
July	79·8	60·1	48·0	41·4	57·5	79·3
August	86·9	66·2	57·0	57·9	71·6	83·8
September	88·6	67·9	56·9	55·1	73·3	83·4
October	84·9	74·2	62·9	62·2	78·7	85·5
November	88·2	80·8	70·4	73·0	82·6	85·4
December	81·7	77·2	70·8	79·7	79·1	82·6

The following Table is the above modified, in which we have replaced $\frac{f}{F}$ by $\frac{f}{H-f}$. In order to avoid decimals, the results have been multiplied by 100,000.

		6.	9.	12.	3.	6.	9.	$\frac{F}{H-f}$.
January ...	Base	410	444	526	560	459	459	380
	Summit ...	473	395	439	458	437	446	514
February..	Base	606	660	727	715	727	696	646
	Summit ...	609	607	671	657	626	626	617
March ...	Base	635	770	862	749	795	814	666
	Summit ...	663	676	715	733	712	688	779
April	Base	842	932	946	945	967	898	876
	Summit ...	740	956	791	807	775	535	687
May	Base	981	1019	1001	1012	979	969	917
	Summit ...	831	868	877	883	868	830	823
June	Base	1248	1268	1291	1290	1278	1497	1106
	Summit ...	973	1036	1099	1130	1094	1023	944
July	Base	1534	1607	1566	1567	1668	1599	1377
	Summit ...	1240	1304	1385	1427	1402	1380	1354
August ...	Base	1482	1588	1581	1611	1808	1663	1318
	Summit ...	1267	1348	1383	1428	1426	1452	1250
September	Base	1269	1472	1460	1435	1499	1418	1137
	Summit ...	1129	1173	1128	1264	1275	1263	1125
October ...	Base	1092	1109	1108	1125	1139	1115	946
	Summit ...	900	896	945	981	985	810	925
November	Base	674	719	770	783	727	714	649
	Summit ...	627	618	650	550	639	630	599
December	Base	644	715	832	930	812	816	765
	Summit ...	658	669	702	729	699	663	665

It will be at once seen from the last Table—

(1) That the hygrometric richness increases from the morning towards midday, or 3 o'clock, and then diminishes as the sun sinks and during the night; this arises from two causes, evaporation during the day and the expansion of the air.

(2) That the richness increases from January to July and August, and then decreases; that it varies from 0·005 to 0·018, that is to say, it is three or four times as much in summer as in winter. We find in like manner that it increases in hot countries, that it is greater even at Laghouat than in Marseilles; and we

must conclude therefore, with Dove, that there is less dry air in summer than in winter in the northern hemisphere.

(3) The hygrometric capacity of the air, that is the maximum vapour which it can contain, is expressed by $\dfrac{F}{H-f}$. But according as we ascend, the temperature and F diminish, while on the other hand H becomes less also. There are two inverse causes of variation; experiment proves that the capacity decreases but very slowly. In like manner the richness is always a little less on the summit than at the base of the Puy de Dôme.

(4) The last column of the table measures the total capacity during the night when the temperature is lowest. It is in general greater than the richness at 6 A.M.; but it is sometimes smaller, from which it may be inferred that the air is saturated at any height when its temperature is a minimum. This explains all the condensations of steam which generally take place in the night.

In fine, the values of $\dfrac{f}{F}$ only tell us the relative degree of dryness or moisture; they do not measure the quantity of vapour. On the other hand, the ratio $\dfrac{f}{H-f}$ gives the hygrometric composition of the air; it shows the changes which take place at day and night, in summer and winter, at various altitudes and in different latitudes.—*Journal de Physique*, vol. iii. p. 469.

ON THE DEFORMATION OF THE LUMINOUS WAVE-SURFACE IN THE MAGNETIC FIELD.   BY E. VON FLEISCHL.

The results of this investigation are summed up by the author as follows :—

1. That the wave-surface in the magnetic field has undoubtedly in general the form described by me of two surfaces of rotation which intersect one another.

2. That the form of these two surfaces differs to an extremely small extent from the spherical form; but that notwithstanding

3. The spherical form of both parts of the double surface which results from Verdet's law of the cosine, and which with this law is implicitly assumed in all previous inquiries, is only a faint approximation to the true form.   And

4. That the form of the wave-surface in the magnetic field is a double surface made up of two ellipsoids of rotation, which are so displaced in the direction of their greatest axes that they nearly coincide with each other.—Wiedemann's *Annalen*, No. 6, 1885.

ON A NEW METHOD FOR DETERMINING THE MECHANICAL EQUIVALENT OF HEAT. BY A. G. WEBSTER.

In 1867 Joule published the results of his experiments for determining the mechanical equivalent of heat, by means of observations on the thermal effect of an electric current. In his experiments a calorimeter was used holding over a gallon of water, the temperature of which was taken by a thermometer. The method about to be described differs from Joule's in that the temperature is measured by the change of resistance of a wire, which is heated by a current, and no water is employed. The idea of the method was suggested by Professor John Trowbridge. Accuracy is not claimed for the results which follow, as the experiments were undertaken only with the view of ascertaining the practicability of the method.

The method of conducting the experiments was as follows :—A thin ribbon of steel, about 45 cm. in length and 1 mm. in breadth, and weighing ·23 gr., was included in one side of a Wheatstone's bridge, by which its resistance was measured. It was then thrown into another circuit, and a transient current from twelve large Bunsen cells was passed through it. The quantity of electricity transmitted was measured by a ballistic galvanometer, and the difference of potential of the ends of the steel strip was compared with the electromotive force of a Daniell's cell by means of a quadrant-electrometer. The rise in temperature of the steel was found by immediately measuring its resistance again. It had been previously found, by a series of experiments made between the temperatures of 90° and 10° C., that the resistance of the steel used was represented by the equation

$$R = a \, (1 + \cdot 00503 \; \theta),$$

θ being the temperature.

If then R_0 be the initial resistance of the strip, and R_1 the resistance after the passage of the current,

$$R_0 = a \, (1 + \beta \, \theta_0),$$

$$R_1 = a \, (1 + \beta \, \theta_1),$$

and the rise in temperature is

$$\theta_1 - \theta_0 = \frac{R_1 - R_0}{a \, \beta}.$$

If w be the weight of the strip, and s its specific heat, the quantity of heat imparted to it by the current is

$$h = ws \, (\theta_1 - \theta_0) = \frac{ws \, (R_1 - R_0)}{a \, \beta}. \quad \dots \dots \dots \quad (1)$$

But if Q is the quantity of electricity transmitted, and E the

difference of potential between the ends of the strip,

$$J\,h = Q\,E,$$

where J is the mechanical equivalent of heat.   We have

$$Q = \frac{H\,T}{G\pi}\,2\sin\frac{a}{2}, \quad \dots\dots\dots\dots\dots\dots \ (2)$$

where a is the first swing of the needle of the ballistic galvanometer, G the galvanometer constant, T the period of a single vibration of the needle, and H the horizontal component of the earth's magnetic force.   G was determined by comparison of the deflections on the scale of the ballistic galvanometer with the readings of a tangent-galvanometer whose constant was calculated, included in the same circuit.   In the experiments, $2\sin\frac{a}{2}$ was considered as proportional to δ, the deflection on the scale, and the value of G for $\delta = 1$ cm. was found to be 769·4.   A shunt was used with the galvanometer, so that the value of Q above given is to be multiplied by $\frac{r+\mathrm{S}}{\mathrm{S}}$, r being the resistance of the galvanometer, and S that of the shunt. The arrangement of the apparatus was as follows :—

R.   The steel strip enclosed in a glass tube to protect it from draughts of air.
W.   Wheatstone's bridge.
G_1.   Thompson astatic galvanometer.
S_1.   Shunt for the same.
G_2.   Ballistic galvanometer.
S_2.   Shunt for the same.
E.   Quadrant-electrometer.
B_1.   Battery of twelve Bunsen cells.
B_2.   Battery of two Leclanché cells.
B_3.   Do.   do.   do.
K_1.   Key for battery B_2 and galvanometer G_1.
K_2.   Key for passing current from B_1 through strip.
K_3.   Key in auxiliary circuit with commutator C, and a second coil of galvanometer G_2, for bringing the needle quickly to rest without heating strip R.

The two galvanometers were arranged to throw their spots of light on the same scale.   The key K_1 was first depressed, R being then in the bridge circuit, and the spot of G_1 was brought to zero by adjusting the resistance c. a was always 1000 ohms, and b one ohm.   On K_1 being raised, a sufficient extra resistance was inserted in c, so that when K_2 was momentarily depressed, and K_1 was immediately afterwards again depressed, the spot G_1 did not move.   The hand soon became accustomed to pressing K_2 just long enough to accomplish this result.   In the experiments, c had to be increased from 1167 ohms by the amount of 50 ohms, and the temperature of the strip accordingly rose about ten degrees.   As

the resistance was measured almost simultaneously with the passage of the current, the rise in temperature could be very exactly known, and the effect of radiation could be very easily determined.
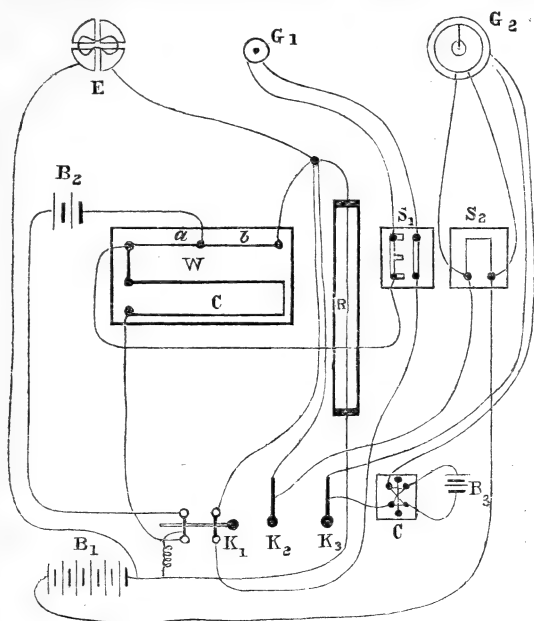
Combining equations (1) and (2), we have

$$J = \frac{E\,H\,T}{G\,\pi}\,\delta\,\frac{(r+S)a\,\beta}{Sws(R_1 - R_0)}.$$

E, as measured by the electrometer, was about one volt, $= 10^8$ C.G.S. units. H was ·171; r, the resistance of the ballistic galvanometer, was 3296 ohms; S_1, the shunt, was 1025 ohms; T, the time of a single vibration of the needle, was 12·6 sec.; a, the resistance of the strip at 0°, was 1·072 ohm; β was ·00503, the weight of the strip was ·230 gr.; its specific heat, ·114; the gain in resistance of the strip was ·05 ohm, and δ, from 20 experiments, was 26·8 cm.; G was 769·4 for $\delta = 1$.

$$J = \frac{10^3 \times ·171 \times 12·6 \times 26·8 \times 4·321 \times 1·072 \times ·00503}{769·4\,\pi\,·05 \times 1·025 \times ·230 \times ·114}$$

$$= 4·14 \times 10^7 \text{ ergs per gram-degree.}$$

In Joule's experiments, the process of heating was continued for nearly an hour, whereas here it lasts for less than a second. In the former method, it was necessary that the current should remain sensibly constant throughout the experiment, and the calorimeter was radiating heat throughout that time. In the short time required by the latter method, the radiation must be very small, and the error from the inconstancy of the curent is avoided. I

intend to undertake a further course of experiments in order to obtain an accurate determination, the purpose of the present paper being merely to show the method.—*Proceedings of the American Academy of Arts and Sciences*, May 26, 1885.

NEW FORM OF HYGROMETER.   BY M. BOURBOUZE.

When vapour begins to condense on a glass plate interposed between the observer and the source of light, concentric rings begin to appear at this point.   They are like those seen round the cloud in foggy weather.

The apparatus we have constructed to produce these rings consists of a small rectangular tube, with small holes on opposite faces closed by very thin glass plates.   A very delicate thermometer is placed so as to dip in only a small quantity of the liquid.   When a current of air is produced in the liquid either by blowing or by aspirating, a deposit of dew rapidly forms on the glass.   If the apparatus is placed between the eye and a point of light, concentric rings are seen about this point, red outside and violet within.   The appearance of the rings as well as the reading of the thermometer may be made from a distance by a telescope.—*Comptes Rendus*, June 22, 1885.

ON THE DISENGAGEMENT OF HEAT IN THE SWELLING AND SOLUTION OF COLLOIDS.   BY E. WIEDEMANN AND CH. LUDEKING.

The conclusions of this research are as follows :—

The solution of the dry colloid is made up of two processes :— (1) hydration, which is attended with disengagement of heat; and (2) solution, which is attended with absorption of heat.— Wiedemann's *Annalen*, No. 6, 1885.

ON A MERCURY-GALVANOMETER.   BY G. LIPPMANN.

A mercury-manometer is placed between the poles of a fixed magnet, which lie right and left of its horizontal arm.   The current traverses the latter in a vertical direction parallel to the axis of the tube, by which the mercury rises in one limb.

If i is the strength of the current, H the strength of the magnetic field, l the length of a small rectangular parallelopipedon in the direction of the current, ϵ its thickness in the direction of the lines of force, the force which displaces the parallelopipedon is Hli, and the pressure $p = \dfrac{\mathrm{H}li}{l\epsilon} = \dfrac{\mathrm{H}i}{\epsilon}$.

Hence the sensitiveness increases with the strength of the magnetic field and the thinness of the column of mercury.   Accordingly the lower bend of the manometer is replaced by a chamber filled with mercury at right angles to the current, and only $\frac{1}{10}$ millim. in thickness.—*Comptes Rendus*, 1884, pp. 1256–57 ; *Beiblätter der Physik*, No. 6, 1885.

XXVII. *Problems on the Distribution of Electric Currents in Networks of Conductors treated by the Method of Maxwell. By* J. A. Fleming, *M.A., D.Sc. (Lond.), Fellow of St. John's College, Cambridge, Professor of Electrical Technology in University College, London*[*].

[Plates VI. & VII.]

§1.　IF any number of points in a plane be joined together by linear conductors such as metallic wires, we have an arrangement of conductors which is called a Network. If at any point in the network a current of electricity be allowed to flow in and is drained off at some other point by conductors, called respectively the anode and kathode conductor, then, after a short period, depending on the self and mutual induction coefficients of the various conductors, the total quantity of electricity arriving by the anode will distribute itself throughout the network and settle down into a steady flow. When this is the case there is a certain definite difference of potential between the anode or source-point and the kathode or sink-point, and there is also a certain definite and constant strength of current in the anode conductor and in every mesh or branch of the network. Call α and γ the potentials of these source- and sink-points, and x the strength of the current in the anode lead, that is the whole quantity of electricity flowing per second through the network, then $(\gamma - \alpha)/x$ measures the resistance of the network. We can imagine the network replaced by a single linear conductor or wire of such sort that if the anode and kathode conductors

are applied to its ends, the difference of potentials at the ends of this simple conductor and the strength of the current flowing through it have the same numerical values γ, α, and x. The resistance of this single conductor is then the same as that of the complex network.

The resistance of the network is obviously some function of the resistances of the separate conductors or wires which compose it, and is capable of being calculated from them. Experimentally, the resistance of a complicated network would best be determined by the measurement of the current-strength in the anode lead and the difference of potential between the source and the sink. Theoretically, it is interesting to examine the law of distribution of currents in a network, and to reduce to a function of the separate resistances the total resistance of the whole network between any two points.

§ 2. In his larger Treatise on Electricity, Clerk Maxwell has treated the general case to determine the differences of potentials and the currents in a linear system of n points connected together in pairs by $\frac{1}{2} n(n-1)$ linear conductors*, and has shown how to form the linear equations, the solution of which gives the condition of the network when given electromotive forces acting along some or all of the branches have established steady currents in them.

The usual method of obtaining a solution for the distribution of currents is the application of Ohm's law round the several currents of the network, controlled by the condition of continuity that there is no creation nor destruction of electricity at the junctions.

Since the publication of the first edition of his Treatise, Maxwell reduced these two sets of equations to one set by the simple device of regarding the real currents in the meshes of the network as the *differences* of imaginary currents round each cycle or mesh of the network, all directed in the same direction, and thus obtained by the application of Ohm's law a single set of linear equations, the solution of which gives the required currents in each branch. Maxwell's method is as follows †:—If we have p points in space and join them together by lines, the least number of lines which will con-

---

* 'A Treatise on Electricity and Magnetism,' 2nd edition, Vol. i. § 280 and § 347.

† This method was first given by Clerk Maxwell in his last course of University lectures. It is alluded to in the second edition of his larger Treatise and in the Appendix of his smaller Treatise by their respective editors, Mr. W. D. Niven and Professor Garnett, to whom it was communicated by the present writer.

nect all the points together is $p-1$. If we add one line more we make a closed circuit somewhere in the system ; that is to say, a portion of space is enclosed and forms a cell cycle or mesh. Every fresh line added then makes a fresh mesh; and hence if there are l lines altogether joining p points, the number of cycles or cells will be $k=l-(p-1)$. Now let such a system of points and lines represent conducting wires joining fixed points, and forming a conducting network. Let a symbol be affixed to each point which represents the electrical potential at that point, and also a symbol affixed to each line representing the electrical resistance of the conductor represented by it. In such a diagram of conductors the form is a matter of indifference so long as the connections are not disturbed and lines are not made to cross unless the conductors they represent are in contact at that point.

Consider a network, Pl. VI. fig. 1, formed by joining nine points by thirteen conductors. Then there will be $13-(9-1)$ $=5$ cycles or cells. Now let an electromotive force E act in one branch B, and give rise to a distribution of currents in the network. Let α, β, γ, δ, &c. represent the potentials at the points, and A, B, C, D, &c. the electrical resistances of the conductors joining these points, and imagine that round each cycle or circuit an imaginary current flows, all such currents flowing in the same direction.

A circuit is considered to be circumnavigated positively when you walk or go round it so as to keep the boundary on your right hand. Hence, going round an area A in the direction of the arrow is positive as regards the inside if you walk inside the boundary-line, and negative as regards external space B if you walk in the same direction round the outside. We shall consider a current, then, as positive when it flows round a cycle in the opposite direction to the hands of a watch. Returning then to the network, we consider that round each cycle flows an imaginary current in the positive direction. The real currents in the conductors are the differences of these in adjacent cycles or meshes, and the imaginary currents will necessarily fulfil the condition of continuity, because any point is merely a place *through* which imaginary currents flow, and at which therefore there can be no accumulation nor disappearance of electricity.

Let x, y, z, &c. denote these imaginary like-directed currents. Then $x-y$ denotes the real current in the branch I, and similarly $x-z$ that in branch H. Then x, y, z, &c. may be called the cyclic symbols of these areas. The cyclic symbol of external space is taken as zero; hence the real current in branch B is simply x.

Let an electromotor act on the branch B, bringing into

existence an electromotive force in that branch.   Let the
internal resistance of the electromotor be included in the
quantity B, representing the resistance of the branch A.   Then
apply Ohm's law to the cycle x formed by the conductors B,
I, H; we have $E - Bx = \gamma - \alpha.$

x is the actual current in this case flowing in the resistance B,
and the potential at the ends of B is equal to the effective
electromotive force acting in it *less* the product of the resist-
ance of the conductor multiplied by the current flowing in it.
For the conductor I we have similarly

$$\gamma - \beta = (x - y)\text{I}.$$

Hence $x - y$ represents the actual current in I : it is the dif-
ference of the imaginary currents flowing round the x and y
cycles in the positive direction.   And for the conductor H
we have also $\beta - \alpha = (x - z)\text{H}.$

Add together these three equations,

$$E = \gamma - \alpha + Bx,$$
$$0 = \beta - \gamma + (x - y)\text{I},$$
$$0 = \alpha - \beta + (x - z)\text{H} ;$$

and we have, as the result of going round the cycle x formed
of conductors B, I, and H,

$$E = x(B + I + H) - y\text{I} - z\text{H}. \quad \ldots \quad (1)$$

α, β, γ have disappeared in virtue of these opposite signs.

This equation (1) is called the equation of the x cycle; and
we see that it is formed by writing as coefficient of the cyclic
symbol x the sum of all the resistances which bound that cycle,
and subtracting the cyclic symbol of each neighbouring cycle
multiplied respectively by the common bounding resistance
as coefficient, and equating this result to the effective electro-
motive force acting in the cycle, written as positive or nega-
tive according as it acts with or against the imaginary current
in the cycle.   This is Maxwell's rule.

Since there are k cycles or meshes we can in this way form
k independent equations, and by the solution of these deter-
mine the k independent variables, x, y, z, &c.   The value of
the current in any branch is then obtained by simply taking
the difference of these variables belonging to the adjacent
meshes, of which the conductor or branch considered is the
common boundary.

§ 3. Let us now consider the most general case possible, in
which we have a network composed of linear conductors suf-
ficiently far apart to have no sensible mutual induction, and
let there be electromotive forces acting in each branch or

conductor. Let the system be considered to have arrived at the steady condition. Let x, y, z, &c. be the cyclic symbols or measure of the imaginary current circulating counter-clockwise round each mesh. Let A, B, C, &c. (fig. 3) be the resistances, and e_1, e_2, e_3, &c. the electromotive forces acting in each branch. These are reckoned positive when they tend to force a current round the mesh counterclockwise, and negative when they act in the opposite direction. Then the equation to the x cycle will be

$$x(A + J + L) - yJ + 0z + 0u + 0w = e_1.$$

The symbols of all the cycles are written down, putting in those of z, u, and w with zero coefficients, as they are not adjacent cycles to that of x. We shall have five equations similar to the above for the other cycles, y, z, w, and u.

Now it can very simply be shown from the theory of determinants, that if there are n linear equations of the type

$$a_1x_1 + a_2x_2 + \quad . \quad . \quad . \quad . \quad . \quad . \quad a_n x_n = p_1,$$
$$b_1x_1 + b_2x_2 + \quad . \quad . \quad . \quad . \quad . \quad . \quad b^n x_n = p_2,$$
$$\vdots \qquad \vdots \qquad\qquad\qquad\qquad\qquad \vdots$$
$$k_1x_1 + k_2x_2 + \quad . \quad . \quad . \quad . \quad . \quad . \quad k_n x_n = p_n,$$

the solution for any variable x_1 is the quotient of the determinants

$$x_1 = \frac{\begin{vmatrix} p_1 & a_2 & . & . & . & . & a_n \\ p_2 & b_2 & . & . & . & . & b_n \\ . & . & & & & & . \\ . & . & & & & & . \\ . & . & & & & & . \\ p_n & k_2 & & & & & k_n \end{vmatrix}}{\begin{vmatrix} a_1 & a_2 & . & . & . & . & a_n \\ b_1 & b_2 & . & . & . & . & b_n \\ . & . & & & & & . \\ . & . & & & & & . \\ . & . & & & & & . \\ k_1 & k_2 & & & & & k_n \end{vmatrix}}$$

The only difference between the numerator and denominator is that the solution for x_n is given by writing as numerator the determinant of the n equations having the column p_1, $p_2 \ldots p^n$ substituted for its nth column, and then writing down as denominator the determinant of the n equations simply.

Thus, for example, the solution of the three linear equations

$$ax + by + cz = d,$$
$$a_1x + b_1y + c_1z = d_1,$$
$$a_2x + b_2y + c_2z = d_2,$$

is

$$x = \frac{\begin{vmatrix} d & b & c \\ d_1 & b_1 & c_1 \\ d_2 & b_2 & c_2 \end{vmatrix}}{\begin{vmatrix} a & b & c \\ a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \end{vmatrix}}$$

with similar expressions for y and z, differing only in having as numerators respectively

$$\begin{vmatrix} a & d & c \\ a_1 & d_1 & c_1 \\ a_2 & d_2 & c_2 \end{vmatrix} \quad \text{and} \quad \begin{vmatrix} a & b & d \\ a_1 & b_1 & d_1 \\ a_2 & b_2 & d_2 \end{vmatrix},$$

denominator being the same.

In this case the evaluation of these determinants is easy : a simple symmetrical process of taking products, according to the rule,

$$\begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} = (aei + bfg + cdh) - (ecg + bdi + afh).$$

§ 4. The properties of determinants enable us, however, very easily to evaluate a numerical determinant of any order. The process consists in the gradual reduction of the determinant in order by such transformations as will render all the elements of the first row or column zero except the first. The determinant is then reduced to the product of its leading elements and the corresponding minor. A repetition of this lowers the determinant one degree at each stage ; and finally, when it is resolved into a numerical two-row determinant, a simple cross multiplication gives its value.

The process of evaluation of a numerical determinant is dependent on four principles :—

(1) That the value of a determinant is not altered if rows are changed into columns.

(2) The interchange of two rows or two columns reverses the sign of the determinant.

(3) If every constituent in any row or column be multiplied by the same factor, then the determinant is multiplied by that factor.

(4) A determinant is not altered if we add to each constituent of any row or column the corresponding constituents of any other row or column multiplied respectively by an identical factor, positive or negative.

For example, suppose that the solution of a series of network equations with numerical coefficients of resistance yield the determinant

$$\begin{vmatrix} 5 & 3 & 1 & 6 \\ 7 & 8 & 9 & 2 \\ 2 & 1 & 4 & 3 \\ 10 & 7 & 5 & 7 \end{vmatrix},$$

we proceed to operate on this as follows :—Subtract the second column from the first and write the remainder. As a new first column we get

$$\begin{vmatrix} 2 & 3 & 1 & 6 \\ -1 & 8 & 9 & 2 \\ 1 & 1 & 4 & 3 \\ 3 & 7 & 5 & 7 \end{vmatrix}.$$

Subtract the third row from the first and put the remainder as a new first row. Also add the third row to the second for a new second row, and we get

$$\begin{vmatrix} 1 & 2 & -3 & 3 \\ 0 & 9 & 13 & 5 \\ 1 & 1 & 4 & 3 \\ 3 & 7 & 5 & 7 \end{vmatrix}.$$

Again, subtract the first row from the third for a new third, and subtract three times the first row from the fourth row for a new fourth row, and we have

$$\begin{vmatrix} 1 & 2 & -3 & 3 \\ 0 & 9 & 13 & 5 \\ 0 & -1 & 7 & 0 \\ 0 & 1 & 14 & -2 \end{vmatrix}$$

which is equivalent to the third order determinant

$$\begin{vmatrix} 9 & 13 & 5 \\ -1 & 7 & 0 \\ 1 & 14 & -2 \end{vmatrix}.$$

And a similar series of operations reduces this to

$$\begin{vmatrix} 76 & 5 \\ 21 & -2 \end{vmatrix}$$

which is equal to

$$-76 \times 2 - 5 \times 21 = -257.$$

Accordingly a series of simple subtractions and multiplications will effect the evaluation of any numerical determinant, and enable us to solve a series of linear network equations for the currents in all the branches when the numerical values of the resistances of the conductors are given. The equations as written above give as solutions the values of the cyclic symbols or imaginary currents round each mesh. To obtain the actual current in any branch, we should have to obtain the values of the cyclic symbols or imaginary currents, for the adjacent meshes of which the given branch is a common boundary. Maxwell ingeniously saves labour in this operation by taking as the symbol for one mesh say $x+y$, and for an adjacent mesh y (fig. 4), and then the real current in the branch AB is

$$x+y-y=x.$$

And the simple rearrangement and solution of the network equation gives at once as value for x the current in the resistance AB, which is the common partition of the two meshes.

§ 5. Returning now to the case when there is only one impressed electromotive force in one branch, we see that in forming the cycle equations only one will be equated to an electromotive force, viz. the equation for the mesh containing the impressed electromotive force in one of its branches. All the other equations will be equated to zero ; and accordingly the equation for the current in any conductor will be of the form

$$x = \frac{E \Delta_{n-1}}{\Delta_n} \; ;$$

where Δ_n is a determinant of the nth order, and Δ_{n-1} is a first minor of this. Referring to fig. 1, we see that, by writing down the five equations of the cycles x, y, z, u, w, we obtain equations by which to calculate the currents in any of the thirteen branches, and the current in branch B will be

$$x = \frac{E \Delta_{n-1}}{\Delta_n} \; ;$$

where Δ_n is the determinant formed of the coefficients of the five equations, and Δ_{n-1} is the first minor corresponding to the coefficient of x in the equation of the x-cycle.

We also saw that if γ and α are the potentials at the ends of the branch B, $\qquad E - Bx = \gamma - \alpha.$

Now consider that part of the network which remains if the conductor B is removed, and let us imagine that a current n continues to be forced into it at γ and drained out at α ; the total resistance of that part of the network, not counting B, is

but this is equal to
$$\frac{\gamma - \alpha}{x} ;$$

$$\frac{E}{x} - B.$$

Now since the resistance of B may be anything, let it be zero; then the total resistance of the network between γ and α will be

$$R = \frac{E}{x} ;$$

but

$$x = \left[\frac{E \Delta_{n-1}}{\Delta_n} \right]_{B=0},$$

where the suffix and bracket denote that after the determinants are formed from the cycle equations, according to Maxwell's rule, then in them B is put equal to zero.

If we denote the determinant of all the n-cycle equations under the condition of $B = 0$ by d_n, and by d_{n-1} the first minor of this or the minor of its leading element corresponding to the coefficient of x with the resistance of the circuit containing the effective electromotive force put equal to zero, we have for the total resistance R of the network between the points at which the current enters and leaves, the expression

$$R = \frac{d_n}{d_{n-1}}.$$

Since, then, as we have seen, the linear equations for the cycles can always be solved by evaluating the determinants, it follows that in all cases, no matter how complicated, the resistance of any network can be calculated by simple arithmetic processes from the given resistances of the branches or conductors which compose it. We have therefore an interesting extension of Maxwell's method of calculating the currents in a network and the potentials at the junctions to a method of calculating the combined resistance of a number of conductors forming a network ; which method consists, as seen above, in forming a certain determinant whose elements are formed of the separate resistances of the branches, and dividing this determinant by another of an order next below, viz. the first minor of its leading elements ; and we find that the resistance between any two points of any network of conductors, however complicated, is expressible as the quotient of a certain determinant by another formed from it.

§ 6. We shall proceed to illustrate this method by a few examples.

1. Find the resistance between the points 1 and 3 (fig. 5) of a network consisting of five conductors, whose resistances are A, B, C, D, E, joining four points, 1, 2, 3, and 4.

Connect 1 and 3 by an imaginary conductor of zero resistance, and having an electromotive force, e, supposed to act in it. Let x, y, z denote the cycles or imaginary like-directed currents in the three meshes so formed, and write down the current equations, according to Maxwell, for these three cycles:—

$$(A+B)x \quad -Ay \quad -Bz \quad =e,$$
$$-Ax \; +(A+E+D)y \quad -Ez \quad =0,$$
$$-Bx \quad -Ey \quad +(B+C-E)z=0.$$

Then, by what has been shown above, the resistance R between the points 1 and 3 of the network is given by the expression

$$R = \frac{\begin{vmatrix} (A+B), & -A, & -B \\ -A, & (A+E+D), & -E \\ -B, & -E, & (B+C+E) \end{vmatrix}}{\begin{vmatrix} (A+E+D,) & -E \\ -E, & (B+C+E) \end{vmatrix}}$$

In dealing with numerical cases we need no longer introduce any notice of imaginary electromotive forces, but proceed according to the following rule.

To determine the resistance of a network of conductors between any two points on the network. Join these two points by a line whose resistance is supposed zero, and give symbols to the meshes of the network so formed; calling this additional mesh produced by the added zero conductor the *added mesh*. Then write down a determinant whose dexter diagonal has for elements the sum of the resistances which bound each mesh, beginning with the added mesh; and for the other elements of each row the resistances which separate this mesh respectively from adjacent meshes, and having the minus sign prefixed, zeros being placed for elements corresponding to nonadjacent meshes.

More explicitly, if we denote by x, y, z, &c. the meshes, x being the added mesh, and by ΣR_x, ΣR_y, ΣR_z, &c. the sum of the resistances which bound each cycle, then these will be the elements along the dexter diagonal of the determinant.

And if x and y are adjacent meshes, and ^{x}R represents the resistance of the common boundary, then $-^x$R will be the element in the xth row and yth column, and also in the yth row and xth column ; but if x and z are nonadjacent meshes, then 0 will be the element in the xth row and zth column, and also in the zth row and xth column. Having formed this determinant, which we call the network determinant, we divide it by the first minor of its leading element; and the quotient is the resistance of the network between the two points, joined by the zero-conductor forming the added mesh. It is seen that, owing to the mode of formation of the network equations, the network determinant is a symmetrical determinant—that is, one half of the determinant is the reflection, as it were, of the other half in the diagonal considered as a mirror.

§ 7. As a means of comparing the results of this method with other known results, let us take the exceedingly simple case of three conductors joining two points in what is commonly called multiple arc.

Let 1, 2, and 3 (fig. 6) be the three conductors joining two points A and B ; let their respective resistances be r_1, r_2, r_3 ; then join A, B by a dotted line so as to make one added mesh, and let the resistance of this added circuit be zero. Then, without writing down the equations to the cycles, we see that the network determinant is

$$d_n = \begin{vmatrix} r_1 & -r_1 & 0 \\ -r_1 & r_1 + r_2 & -r_2 \\ 0 & -r_2 & r_2 + r_3 \end{vmatrix}$$

The elements r_1, $r_1 + r_2$, $r_2 + r_3$ of the dexter diagonal are the sums of the resistances which bound each mesh, x, y, and z, taking the added mesh x first.

The other elements of the first row are the resistances, with minus sign prefixed, which separate the mesh x from mesh y and mesh z ; or are common to x and y and x and z, viz. r_1 and zero, because x and z are nonadjacent. And, similarly, if m and n are any two meshes, then the element in the nth row and mth column is the resistance separating or common to the two meshes ; and the element in the nth row and mth column is identical with that in the mth row and nth column : zero being placed as an element if these meshes, m and n, have no common boundary or circuit.

The above determinant is easily evaluated. By adding the first row to the second for a new second row, and this new second row to the third for a new third row, we transform the

determinant easily into

$$\begin{vmatrix} r_1 & -r & 0 \\ 0 & r_2 & -r_2 \\ 0 & 0 & r_3 \end{vmatrix}$$

which is equal to

$$r_1 r_2 r_3.$$

The first minor of the leading term of the network determinant is

$$\begin{vmatrix} r_1 + r_2 & -r_2 \\ -r_2 & r_2 + r_3 \end{vmatrix} = d_{n-1},$$

which is equal to

$$r_1 r_2 + r_2 r_3 + r_3 r_1 \; ;$$

and hence the resistance of the network between A and B is

$$\frac{d_n}{d_{n-1}} = \frac{r_1 r_2 r_3}{r_1 r_2 + r_2 r_3 + r_3 r_1},$$

which is a known result. In these simple cases the above general rule is, of course, a less easy method of finding the combined resistance than the direct application of Kirchhoff's corollaries of Ohm's law ; but whereas the general method is alike applicable to the most complicated as well as to the most simple cases, the simple direct method requires twice as many equations, and does not determine the direction as well as magnitude of the current in each branch.

§ 8. As a simple numerical example we may take the case of a crossed square of wires. Let 12 conductors join 9 points (fig. 7) so as to form a square divided into four squares, or a four-mesh network of conductors. Let the resistance of each branch, as *ab*, be unity. It is required to find the combined resistance between A and B. Number the meshes 1, 2, 3, 4, 5 ; 1′ being the added mesh formed by joining A B by a dotted line, making an additional fifth mesh, the resistance of this additional ideal conductor being zero. Then the network determinant is

$$\begin{vmatrix} 4 & -1 & -2 & -1 & 0 \\ -1 & 4 & -1 & 0 & -1 \\ -2 & -1 & 4 & -1 & 0 \\ -1 & 0 & -1 & 4 & -1 \\ 0 & -1 & 0 & -1 & 4 \end{vmatrix} = d_n.$$

The dexter diagonal has for each element 4, viz. the sum of the four resistances, each to unity, which form each mesh or cell. And all the other figures, say, in the nth row, are the resistances (with minus sign prefixed) separating the nth mesh from all other meshes, zero being placed in the column corresponding to any mesh which has no common conductor or branch with this nth mesh. The order in which the columns stand and also the rows correspond to the order in which the meshes are numbered in fig. 7.

The numerical value of this determinant is easily found to be $288 = 3 \times 96 = d_n$. Now if we take the first minor of its leading element, we get a determinant formed of the elements included in the dotted rectangle ; and taking this as a separate determinant and evaluating it, we have its value

$$d_{n-1} = 192 = 2 \times 96 ;$$

hence the resistance of the network between the points A and B is

$$\frac{d_n}{d_{n-1}} = \frac{288}{192} = 1\tfrac{1}{2} \text{ units.}$$

§ 9. One more simple numerical case may be taken and compared with the results of known methods.

Let a hexagon of conductors be taken (fig. 8) having crossed diagonals all meeting in the centre. Let the resistance of each side, as ab, be unity, and also let the resistance of each semidiagonal, as $0a$, be unity. · Then required the combined resistance of this network of 12 conductors between the points A and B diametrically opposite. Join the points A and B by a dotted line of zero resistance, making an added mesh 1. Mark the other meshes 2, 3, 4, 5, 6, 7. Then by forming the network equations it is easily seen that the network determinant d^n is

$$
\begin{vmatrix}
3 & -1 & -1 & -1 & 0 & 0 & 0 \\
-1 & 3 & -1 & 0 & -1 & 0 & 0 \\
-1 & -1 & 3 & -1 & 0 & 0 & 0 \\
-1 & 0 & -1 & 3 & 0 & 0 & -1 \\
0 & -0 & 0 & 0 & 3 & -1 & 0 \\
0 & 0 & 0 & 0 & -1 & 3 & -1 \\
0 & 0 & 0 & -1 & 0 & -1 & 3
\end{vmatrix} = d_n.
$$

The value of this determinant is 256.

say, adjacent angles of the hexagon, in which case no such simple direct method as employed above can be used.

§ 10. The following example will give a good illustration of Maxwell's method of treating network problems, viz. the case of Sir W. Thomson's resistance-balance for small resistances. In this arrangement (fig. 10) 9 conductors join 6 póints and form 4 cells. B is the battery-circuit in which operates an electromotive force E. Let the four cycle currents be denoted by $x+y$, y, z, and w. These are the imaginary like-directed currents round the circuits, and the real currents in the branches are the differences of these.

The problem is to determine the current in the galvanometer branch G, and the relation of the resistances when this current through G is zero. Let P, Q, S, T, R, r, D be respectively the resistances of the branches, and G the resistance of the galvanometer circuit, and B the resistance of the battery circuit. Then $x+y$ and y being the imaginary like-directed currents in the two adjacent meshes of which the galvanometer branch is the common boundary, then $x+y-y=x$ is the current through the galvanometer.

Proceeding to write down the cycle equations, according to Maxwell's rule, we have

$$(P+G+Q+R)\overline{x+y}-Gy-Qz-Rw=0,$$
$$(T+r+S+G)y-G\overline{x+y}-Sz-rw=0,$$
$$(Q+S+D)z-Sy-Q\overline{x+y}-Dw=0,$$
$$(R+O+r+B)w-R\overline{x+y}-Oz-ry=E.$$

Rearranging these equations and solving for x, we have the ollowing value :—

$$x=\frac{E}{\Delta}\begin{vmatrix} -\overline{Q+S}, & D, & -D \\ T+S+r, & T+r, & -r \\ P+Q+R, & P+Q, & -R \end{vmatrix},$$

in which Δ is the determinant of the four equations in x, y, z, and w, and whose specific value does not concern us.

This gives the current in the galvanometer-branch ; and if this is zero, then the determinant in the numerator of the equation giving x must be zero. Hence, when x is zero, we have

$$\begin{vmatrix} -\overline{Q+S}, & D, & O \\ T+S+r, & r+T, & T \\ P+Q+R, & P+R, & P \end{vmatrix}=0,$$

this determinant being derived from the one in the equation for x by adding the second and third columns for a new third column.

This last determinant equation writes out into

$$(Q+S+D) \begin{vmatrix} T, & r \\ P, & R \end{vmatrix} + D \begin{vmatrix} T, & S \\ P, & Q \end{vmatrix} = 0.$$

Hence the condition that the current in the galvanometer-branch shall be zero is that both determinants in this expression shall be simultaneously zero, or

$$\begin{vmatrix} T, & r \\ P, & R \end{vmatrix} = 0, \quad \text{and} \quad \begin{vmatrix} T, & S \\ P, & Q \end{vmatrix} = 0 ;$$

that is,

$$\frac{T}{P} = \frac{r}{R} = \frac{S}{Q}.$$

Hence this condition expresses the relation which must hold good between the magnitudes of the resistances T, P, Q, S, r, R, in order that the galvanometer-branch G may be conjugate to the battery-branch B.

The above example shows well the symmetry of the method when dealing with a case of distribution of currents in a network.

§ 11. As a final illustration, let us consider the case of a circular wire A P B Q, with a diametral wire P Q across it.

Take any two points A, B, at the extremities of a diameter not coinciding with P Q, but separated by an angular distance θ from it, and let us obtain the resistance of the circular wire so crossed between the points A and B.

Join the points A, B by a dotted line of zero resistance. Call the three meshes so formed x, y, and z ; let r be the radius of the circle ; and let ρ be the electrical resistance of the wire per unit of length.   Then the

Resistance of branch PQ $= 2\rho r$,
        ,,   ,,   AP $= \rho r \theta$,
        ,,   ,,   AQ $= \rho r (\pi - \theta)$,

and

Resistance of branch BQ $=$ resistance of AP,
        ,,   ,,   PB $=$,,   ,,   AQ.

Then the network determinant d_n is

$$\begin{vmatrix} \rho r \pi, & -\rho r (\pi - \theta), & -\theta \\ -\rho r (\pi - \theta), & \rho r (\pi + 2), & -\rho r 2 \\ -\theta, & -\rho r 2, & \rho r (\pi + 2) \end{vmatrix}.$$

Removing the common factor $r\rho$, we have to evaluate

$$\begin{vmatrix} \pi & -\overline{\pi-\theta} & -\theta \\ -\overline{\pi-\theta} & \pi+2 & -2 \\ -\theta & -2 & \pi+2 \end{vmatrix}.$$

This is very easily reduced to

$$\pi \begin{vmatrix} 0 & \theta & \pi \\ -1 & 1 & 2 \\ -\theta & 2 & \pi \end{vmatrix},$$

which is equal to

$$2\pi(\pi+\theta\pi-\theta^2),$$

and therefore

$$d_n = r^3\rho^3 2\pi(\pi+\theta\pi-\theta^2).$$

The value of the minor of the leading element of the network determinant, viz. d_{n-1}, is

$$r^2\rho^2\{(\pi+2)^2-4\} = r^2\rho^2\pi(\pi+4).$$

Hence the resistance of the network between A and B, $=$ R, is

$$\frac{d_n}{d_{n-1}} = \mathrm{R} = r\rho\,\frac{2\pi(\pi+\theta\pi-\theta^2)}{\pi(\pi+4)}$$

$$= r\rho\,\frac{2\pi+2\pi\theta-2\theta^2}{\pi-4}.$$

We can check this in the extreme cases when $\theta=0$ or $\theta=\frac{\pi}{2}$.

When $\theta=0$, the network-resistance is simply that of three conductors whose resistances are $2\rho r$, $\pi\rho r$, and $\pi\rho r$ joined in multiple arc, as in Plate VII. fig. 12, because PQ now coincides with AB; and this is simply $r\rho\dfrac{2\pi}{\pi+4}$. It is seen at once that the above value for R becomes this when θ is put equal to zero. Now, when $\theta=\frac{\pi}{2}$, the diameter PQ joins points at equal potential (fig. 13), and is not traversed by any current at all; and hence its removal will not affect the resistance between the points A and B.

Hence the resistance of the network simply reduces to that of a circle measured at the ends of a diameter, or to two conductors of resistance $\pi\rho r$ joined in multiple arc, and this is equal to $\rho r\dfrac{\pi}{2}$. By putting $\theta=\frac{\pi}{2}$ in the general solution for R above, we get it reduced to $r\rho\dfrac{\pi}{2}$; and accordingly this

formula agrees, as it should do in these reduced cases, with the results of the direct method based on first principles. If a value of θ be found which will make the expression

$$2\pi + 2\pi\theta - 2\theta^2$$

equal to $\pi + 4$, then for such a position of the diameter AB relatively to PQ the resistance of the circle and its diagonal PQ would be exactly equal to the resistance of half the diametral wire or to its radius, assuming both the circle and diagonal to be made of wire of equal conductivity per unit of length. To find the value of θ for which this is the case, we have to solve the quadratic

$$2\pi + 2\pi\theta - 2\theta^2 = \pi + 4.$$

If we put $\theta = \dfrac{\pi}{180} x^{\circ}$, where x° is the number of degrees equivalent to the angle θ, we find, as a solution for this quadratic, that the positive root is nearly

$$171^{\circ}\!\cdot\!804.$$

Now 3 radians, or 3 unit-angles in circular measure, are nearly

$$171^{\circ}\!\cdot\!887.$$

Hence, for a position of the diagonal PQ as in fig. 14, when the arc AP is nearly equal to $\pi - 3$, or to the fractional part of π, the resistance of the circle and diagonal PQ measured between the points A, B is very nearly equal to that of half the diagonal PQ; or, which is the same thing, the resistance of PQ alone is nearly double the combined resistance of the circle and diagonal measured between the points A and B at the extremity of a diameter removed $171^{\circ}\!\cdot\!804$ from PQ.

§ 12. A small practical application of this last example may be made in constructing a variable resistance.

Let PAQB (fig. 15) be a narrow circular canal cut in a slab of wood or ebonite and filled with mercury. Let PDQ be a bent copper wire balanced on a pivot CD, and having its ends P and Q dipping in the trough at opposite extremities of a diameter of the circular trough PAQB.

The total resistance between any two points A and B in the trough, which are also diametrically opposite, can be varied within limits by changing the position of PQ relatively to AB.

When PQ is turned so that it is at right angles to the diameter AB, it does not affect the total resistance between A and B, and may be removed. The resistance is then just that of the circular band of mercury taken at opposite extremities of its diameter. When PQ is coincident with AB it reduces the resistance, and in intermediate positions the joint resistance

of trough and diagonal wire is intermediate between the greatest and least when it is in position removed either 90° or 0° from AB.

By using a circular glass canal filled with sulphate-of-zinc solution, and a zinc diagonal electrode and amalgamated-zinc electrodes at A and B, a variable resistance may be constructed capable of being varied over considerable ranges perfectly gradually and with no imperfect contacts.

§ 13. Having illustrated, by the foregoing examples, the methods of calculating both the currents in and resistances of networks of any complexity, we return for a moment to some general considerations.

Consider a function formed of the sum of each separate resistance in a network multiplied by the square of the current strength flowing through it. This expresses the heat generated per second in the whole network by that distribution of current. This is called the Dissipation Function of the network. It represents the rate at which energy is being transformed into heat or rendered unavailable.

Write down the dissipation function for the network in fig. 1. Call it H. Then

$$H = Bx^2 + I\overline{x-y}^2 + H\overline{x-r}^2 + Cy^2 + L\overline{z-y}^2 + Az^2 + J\overline{u-y}^2$$
$$+ K\overline{z-w}^2 + (D+E)u^2 + (F+G)w^2 + M\overline{u-w}^2.$$

Now the cycle equation for the cycle or mesh y is, by Maxwell's rule,

$$(C+I+L+J)y - Ix - Lz - Ju = 0,$$

which is the same as

$$Cy - I\overline{x-y} - L\overline{z-y} - J\overline{u-y} = 0.$$

And this is at once seen to be identically the same as the first partial differential of the dissipation function with respect to the cyclic symbol y, or is the same as

$$\tfrac{1}{2}\frac{\partial H}{\partial y} = 0,$$

where ∂ represents partial differentiation ; and by writing down the other cycle equations for each cyclic symbol or imaginary current, x, y, z, &c., we can show that these current-equations are respectively

$$\tfrac{1}{2}\frac{\partial H}{\partial x}, \quad \tfrac{1}{2}\frac{\partial H}{\partial y}, \quad \tfrac{1}{2}\frac{\partial H}{\partial z}, \&c.,$$

each equated to the effective electromotive force in that cycle or mesh.

Let us assume now that x is constant, but that y, z, u, w, &c. are independent variables and are arbitrarily changed. This is equivalent to supposing that a given quantity of electricity per second is pushed into the network, but that its distribution is supposed to be varied. We see that the equations which we write down, according to Maxwell, to determine the *real* distribution of currents in the network, according to Ohm's law, are the same equations as would be written down to find the values of y, z, u, w, &c., which make the dissipation function a minimum under fixed conditions of total current flowing into the network, viz. equating to zero the first partial differentials of H with respect to the variables y, z, u, &c. The same holds good generally, hence we see that this is another way of arriving at the theorem of which Maxwell has given a proof on page 375, § 284, vol. i. of his large Treatise, 2nd edition, viz.:—" In any system of conductors in which there are no internal electromotive forces the heat generated by currents distributed in accordance with Ohm's law is less than if the currents had been distributed in any other manner consistent with the actual conditions of supply and outflow of the current."

The exact proof that the partial differentials of the dissipation function equated to zero gives the condition that the dissipation function shall be a *minimum* is not complete without an examination of Lagrange's conditions. It is obvious that the second partial differentials of the dissipation function are quantities which are resistances, viz. the coefficients of the current symbols in the cycle equations, and that the conditions for a minimum are complied with, since $\dfrac{\partial^2 H}{\partial y^2}$, &c. are positive ; and the *discriminant* of the quadratic function of the currents or symmetrical determinants formed of these second partial differentials is what has been called above the network determinant. This and all its successive minors are positive quantities [*].

§ 14. In the foregoing sections the problems have been treated under the limitations that the various meshes of the network of conductors have no mutual and no self-induction. The introduction of these inductive actions will affect in a considerable way the treatment of the problem ; and the dis-

---

[*] See Williamson's ' Differential Calculus,' p. 408, " On the Conditions for a Maximum and Minimum of a Function of any number of Variables," § 163, and Appendix.

tribution of the currents in, and the resistance of, the network will be affected by them during the time taken by the currents to become steady.

In those pages of his Treatise in which Clerk Maxwell worked out his splendid dynamical theory of electromagnetism, he starts with the explanation of the methods Lagrange and Hamilton employed to bring pure dynamics under the power of analysis, and the results of Lagrange are embodied in the equation

$$X = \frac{d}{dt}\frac{dT}{d\dot{x}} - \frac{dT}{dx},$$

in which X is the impressed force tending to increase the variable x, and T denotes the visible energy of the system of bodies at that instant.

This equation establishes a relation between the kinetic energy of a material system at any instant, the force impressed upon it in a certain direction, and a quantity called a variable, which expresses the state or condition of the system with respect to that direction. Maxwell, by a process of extraordinary ingenuity, extended this reasoning from materiomotive forces, masses, velocities, and kinetic energies of gross matter to the electromotive forces, quantities, currents, and electrokinetic energies of electrical matter, and in so doing obtained a similar equation of great generality for attacking electrical problems.

In the electrical problem the variables are the quantities of electricity x, y, z, &c. which have from the beginning of the epoch flowed past any points, and the analogues of the velocities are the fluxes of these, $\dot{x}$, $\dot{y}$, $\dot{z}$, &c., or the currents.

The electrokinetic energy is measured by the quadratic expression

$$T = \tfrac{1}{2}L_1\dot{x}_1^2 + \tfrac{1}{2}L_2\dot{x}_2^2 + \ \ldots \ M_{12}\dot{x}_1\dot{x}_2 + , \ \&c.,$$

where the coefficients L_1, L_2, M_{12} are functions of the geometrical variables, but into which the electrical variables do not enter.

If now, as before, $\dot{x}_1$, $\dot{x}_2$ represent the imaginary like-directed currents round each mesh of a network, in which currents are beginning to flow, then

$$\frac{dT}{d\dot{x}_1} \text{ and } \frac{dT}{d\dot{x}_2}, \&c.$$

represent the electrokinetic momenta of these circuits. Denote them by p_1, p_2, &c., and accordingly

$$p_1 = L_1 \dot{x}_1 + M_{12} \dot{x}_2, \text{ \&c.}$$

If E is the impressed electromotive force in the circuit or mesh arising from some cause, battery, thermopile, dynamo machine, &c., which would produce a current independently of magneto-induction, then, if R be the total resistance round the mesh, and $\dot{x}$ the cyclic current, $R\dot{x}$ is the electromotive force required to overcome the resistance of the circuit, and $E - R\dot{x}$ is the electromotive force available for changing the electric momentum of the circuit.

Accordingly, by Lagrange's equation,

$$E - R\dot{x} = \frac{dp}{dt} - \frac{dT}{dx},$$

where T is the electrokinetic energy. As T does not contain x, that is to say it is a function of currents, not quantities, the last term disappears, and we have

$$E - R\dot{x} \quad \frac{d}{dt} \frac{dT}{d\dot{x}},$$

or

$$\frac{d}{dt} \frac{dT}{d\dot{x}} + R\dot{x} = E.$$

The electromotive force is therefore expended in two things : first, overcoming the resistance R ; and, secondly, increasing the electromagnetic momentum p. Now if there is no electromagnetic momentum, we have seen that the cyclic equations are of the form

$$\tfrac{1}{2}\frac{dH}{d\dot{x}} = E',$$

where H is the dissipation function of the system, and E′ is the acting electromotive force concerned in overcoming the resistance of the circuit.

If, then, we substitute for $R\dot{x}$ in equation $\tfrac{1}{2}\dfrac{dH}{d\dot{x}}$, we have as the general equation for the electromotive force in any mesh or cycle x,

$$\frac{d}{dt} \frac{dT}{d\dot{x}} + \tfrac{1}{2}\frac{dH}{d\dot{x}} = E.$$

This most important equation is Maxwell's general equation for determining the current $\dot{x}$ in any circuit when the dissipation function, and kinetic energy, and impressed electro-

motive force are known. We shall proceed to apply it to the solution of some network problems, in which the self and mutual induction of the branches is taken into account to determine the distribution of currents and combined resistance at any instant during the variable state.

§ 15. Consider, first, the case of a galvanometer with a coefficient of self-induction L and resistance G, and shunted by a shunt of resistance S, but wound so as to have no co-efficient of self-induction, and let the shunt and galvanometer-coils be so far removed that there is no coefficient of mutual induction. This is the ordinary practical case.

Let a battery be joined up and let the battery and connections have a resistance B and electromotive force E (see fig. 16).

We have then a two-mesh network. Call the current in the galvanometer- and shunt mesh y and the current in the shunt and battery mesh $x+y$. Then the current through the galvonometer is y, the current through the shunt is x, and the current through the battery is $x+y$.

The dissipation function H is

$$B\overline{x+y}^2 + Sx^2 + Gy^2 = H,$$

which may be written

$$\overline{B+S}\ \overline{x+y}^2 + \overline{G+S}\ y^2 - 2S\overline{x+y}\,y = H\ ;$$

and the electromagnetic energy is

$$\tfrac{1}{2}Ly^2 = T.$$

Hence, by the general equation,

$$\frac{d}{dt}\frac{dT}{dy} + \tfrac{1}{2}\frac{dH}{dy} = E,$$

we have the two cycle equations for the y and $x+y$ cycles,

$$\left.\begin{array}{c} \dfrac{d}{dt}Ly + \overline{G+S}y - S\overline{x+y} = 0 \\[2mm] \overline{B+S}\ \overline{x+y} - Sy = E, \end{array}\right\}$$

and

or

$$\left.\begin{array}{c} \left(L\dfrac{d}{dt}+G\right)y - Sx = 0, \\[2mm] By + \overline{B+S}\,x = E. \end{array}\right\}$$

and

The solution of these for x and y is

$$y = \frac{\begin{vmatrix} E & B+S \\ 0 & -S \end{vmatrix}}{\begin{vmatrix} B & B+S \\ L\dfrac{d}{dt}+G & -S \end{vmatrix}} = \text{current through [galvanometer,}$$

and

$$x = \frac{\begin{vmatrix} B & E \\ L\dfrac{d}{dt}+G & 0 \end{vmatrix}}{\begin{vmatrix} B & B+S \\ L\dfrac{d}{dt}+G & -S \end{vmatrix}} = \text{current through [the shunt.}$$

Writing out this differential equation for y' we have,

$$\begin{vmatrix} L\dfrac{d}{dt} & -G \\ 0 & B+S \end{vmatrix} y + \begin{vmatrix} B & B+S \\ -G & S \end{vmatrix} y = \begin{vmatrix} E & -\overline{B+S} \\ 0 & S \end{vmatrix},$$

or

$$\overline{B+S}\, L\frac{dy}{dt} + (BS + RG + SG)y = ES,$$

or

$$\frac{dy}{dt} + \frac{BS+BG+SG}{(B+S)L}\, y = \frac{ES}{(B+S)L}.$$

The solution of this differential equation is

$$y = \frac{ES}{BG+GS+BS}\left(1 - e^{-\frac{BG+GS+BS}{(B+S)L}\, t}\right).$$

This gives the value of the current through the galvanometer at any time, t, after starting the flow by making the connection with the battery.

When $t=0$, then $y=0$, and as t increases y increases, and finally, when $t=\infty$, $y = \dfrac{ES}{BG+GS+BS}$, or, as it may be written, $y = \dfrac{S}{G+S}\,\dfrac{E}{B+\dfrac{SG}{G+S}}$.

This last is the ordinary formula given for the current through a shunted galvanometer; but we see that when self-induction is taken into account, it is not until after an infinite time that the current rises to this value.

By the cycle equation, $By + \overline{B+S}x = E$: hence

$$x = \frac{E - By}{B + S}.$$

And if we write N for the factor $\left(1 - e^{-\frac{BG + GS + BG}{(B+S)L}t}\right)$, then

$$x = \frac{E - \dfrac{EBSN}{BG + BS + SG}}{B + S}$$

$$= \frac{E(BG + BS + SG - BSN)}{(B+S)(BG + BS + SG)} \, ;$$

which gives the current through the shunt at any instant.

§ 16. Consider now the combined resistance of the galvanometer and shunt at any instant.

The self-induction of the galvanometer acts like a spurious resistance during the commencement of the current and drags out or prolongs the rise of current in the galvanometer-coils ; accordingly, during this period the combined resistance is a function of the time t from the commencement of the flow.

To calculate the combined resistance of galvanometer and shunt at any instant, we proceed as in the cases above exemplified. Form the cycle equations

$$(B + S)\overline{x + y} - Sy = E,$$

$$-S\overline{x + y} + \left(G + S + L\frac{d}{dt}\right)y = 0.$$

Write down the determinant of these equations with the battery-circuit resistance put equal to zero, that is put B=0, and the combined resistance R required is the quotient of this determinant by its first minor, viz.

$$R = \frac{\begin{vmatrix} S & -S \\ -S & G + S + L\dfrac{d}{dt} \end{vmatrix}}{G + S + L\dfrac{d}{dt}},$$

or

$$R = \frac{\begin{vmatrix} S & 0 \\ -S & G + L\dfrac{d}{dt} \end{vmatrix}}{S + G + L\dfrac{d}{dt}} = \frac{S\left(G + L\dfrac{d}{dt}\right)}{S + \left(G + L\dfrac{d}{dt}\right)}.$$

We have now to see what is the meaning of $G + L\dfrac{d}{dt}$ as an operator in a determinant.

If we consider the formation of a current in a circuit of resistance R and coefficient of self-induction L by an electro-motive force E, we have the equation for the current i

$$L\frac{di}{dt} + Ri = E.$$

Write thus

$$\left(L\frac{d}{dt} + R\right)i = E\;;$$

or, by notation of the calculus of operations,

$$i = E\left(L\frac{d}{dt} + R\right)^{-1}.$$

But now the solution of the above differential equation under the conditions $t=0$, $i=0$, and $t=\infty$, $i=\dfrac{E}{R}$, is

$$i = E\frac{\left(1 - e^{-\frac{R}{L}t}\right)}{R}.$$

Comparing these two expressions for i together, we have

$$L\frac{d}{dt} + R = \frac{R}{\left(1 - e^{-\frac{R}{L}t}\right)}.$$

Hence we may substitute in the expression for the combined resistance of galvanometer and shunt for $L\dfrac{d}{dt} + G$,

$$\frac{G}{\left(1 - e^{-\frac{G}{L}t}\right)},$$

and we have as a result,

$$R = \frac{SG}{G + S\left(1 - e^{-\frac{G}{L}t}\right)}.$$

We see that when $t=0$, $R=S$, and when $t=\infty$, $R=\dfrac{GS}{G+S}$.

Hence the result shows that at the first instant of starting a current through a shunted galvanometer, when the shunt has no self-induction and the galvanometer a considerable one, the galvanometer behaves as if it had a high spurious resistance, which in time dies away, allowing the total current, after an infinite time, to be divided between the galvanometer and the shunt in the ratio of $\dfrac{S}{G+S}$ to $\dfrac{G}{G+S}$.

§ 17. We may apply the same methods to the examination of the case when the current sent through the shunted galvanometer is not generated by a source of constant electromotive force, but is a discharge from a condenser.

Let K (fig. 17) be a condenser connected up with a shunted galvanometer, so that when the key k is pressed a discharge passes through the galvanometer and shunt. Call the two cycles x and y. Let G be the galvanometer-resistance and S the shunt, and let L_1 and L_2 be their respective coefficients of self-induction ; the coefficient of mutual induction being zero.

Let q be the quantity of electricity in the condenser at any instant t. Counting the time from the instant of commencing the discharge, let C be the capacity of the condenser, and let q_1 and q_2 be the quantities of electricity which have, since the beginning of the epoch, flowed respectively through the galvanometer and the shunt.

If T be the energy function and F the dissipation function, we have, as above, the fundamental equations

$$2T = L_1 y^2 + L_2 (x-y)^2,$$

and

$$2F = G y^2 + S(x-y)^2 ;$$

or

$$2T = L_1 y^2 + L_2 x^2 + L_2 y^2 - 2 L_2 xy,$$
$$2F = G y^2 + S x^2 + S y^2 - 2 S xy.$$

By the fundamental equation

$$\frac{d}{dt} \frac{dT}{dx} + \frac{dF}{dx} = e.$$

For e we must write $\dfrac{q}{C}$.

Writing, then, the cycle equations, we have

$$\frac{d}{dt}(L_2 x - L_2 y) + S x - S y = \frac{q}{C}.$$

$$\frac{d}{dt}(L_1 y + L_2 y - L_2 x) + G y + S y - S x = 0 ;$$

from which we deduce easily

$$L_1 \frac{dy}{dt} + G y = \frac{q}{C},$$

and

$$L_2 \frac{d}{dt}(x-y) + S(x-y) = \frac{q}{C} ;$$

or

$$L_1 \frac{dy}{dt} - L_2 \frac{d}{dt}(x-y) = S(x-y) - Gy.$$

Now y and $x-y$ represent the strengths of the currents flowing through the galvanometer and the shunt at any instant.

If we integrate both sides of the equation from 0 to ∞, we have

$$\left[L_1 y - L_2(x-y) \right]_0^\infty = S \int_0^\infty \overline{x-y} dt - G \int_0^\infty y dt.$$

Now the left-hand side of the equation is zero because quantities of the form of Ly represent the number of lines of force which are added into the circuit of the galvanometer, and the discharge may be divided into two parts, during one of which lines of force are being added to, and in the other of which subtracted from, the circuits of the galvanometer and shunt; and the sum of these is zero. Again, $\int_0^\infty (x-y) dt$ and $\int_0^\infty y dt$ represent the whole quantities q_2 and q_1 of electricity which have flowed respectively through the galvanometer and the shunt.   Hence we arrive at the conclusion that

$$S q_2 - G q_1 = 0,$$

or

$$\frac{G}{S} = \frac{q_2}{q_1};$$

that is, the total quantity of the discharge is divided between the two circuits inversely as their resistances.   We see therefore that self-induction does not affect the ratio of division of a discharge in a divided circuit, provided that no external work, such as the moving of magnets or circuits conveying currents, absorbs current energy.   Hence, if a ballistic galvanometer is shunted and a discharge sent through it, if the needle has sufficient moment of inertia and the discharge is sufficiently short, so that the needle has not perceptibly moved from its position before the discharge is over, then the whole quantity of electricity is divided between the galvanometer and the shunt in the inverse ratio of their resistances.

§ 18. To complete the solution we have to calculate the current flowing through the galvanometer and shunt at any instant.

Taking the two cycle equations

$$L_1 \frac{dy}{dt} + Gy = \frac{q}{C}, \quad \cdots \quad \cdots \quad \cdots \text{(i.)}$$

and

$$L_2 \frac{d}{dt}\overline{x-y} + S\overline{x-y} = \frac{q}{C}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \text{(ii.)}$$

we get

$$L_1 \frac{dy}{dt} = \frac{q}{C} - Gy,$$

and

$$L_1 L_2 \frac{dx}{dt} = (L_1 + L_2)\frac{q}{C} - L_1 S\overline{x-y} - L_2 Gy$$

$$= (L_1 + L_2)\frac{q}{C} - L_1 Sx + (L_1 S - L_2 G)y. \quad \cdot \quad \text{(iii.)}$$

Differentiate this last equation with regard to t and eliminate $\frac{dy}{dt}$ by the help of the equation above it, and we arrive at

$$L_1 L_2 \frac{d^2x}{dt^2} = -L_1 S\frac{dx}{dt} + \frac{L_1 S - L_2 G}{L_1}\left(\frac{q}{C} - Gy\right).$$

Eliminating y between the last and equation (iii.) and reducing, we arrive at

$$L_1 L_2 \frac{d^2x}{dt^2} + (L_1 S + L_2 G)\frac{dx}{dt} + GSx = (G+S)\,\frac{q}{C};$$

but now $x = -\frac{dq}{dt}$. Making this substitution we have

$$L_1 L_2 C \frac{d^3q}{dt^3} + C\,(L_1 S + L_2 G)\frac{d^2q}{dt^2} + CGS\frac{dq}{dt} + (G+S)q = 0, \quad \text{(iv.)}$$

an interesting equation, the solution of which gives us the quantity of electricity in the condenser at any instant, t, after starting the discharge. According to the equation above

$$L_1 \frac{dy}{dt} + Gy = \frac{q}{C}.$$

This equation gives us a value of y or the current through the galvanometer at any instant when we know q, or the quantity left in the condenser at that instant. The above may be written

$$y = \left(L_1\frac{d}{dt} + G\right)^{-1}\frac{q}{C},$$

and the final equation (iv.) may be written

$$\frac{q}{C} = \left(L_1 L_2 C^2 \frac{d^3}{dt^3} + (L_1 S + L_2 G)C^2 \frac{d^2}{dt^2} + C^2 GS \frac{d}{dt} + C(G+S)\right)^{-1} 0;$$

and accordingly we have the following equation for the value of y at any instant

$$y = \left(L_1 \frac{d}{dt} + G \right)^{-1} \left(L_1 L_2 C^2 \frac{d^3}{dt^3} + (L_1 S + L_2 G) C^2 \frac{d^2}{dt^2} + C^2 G S \frac{d}{dt} + C(G+S) \right)$$

which may be written

$$y = \left(L_1^2 L_2 C^2 \frac{d^4}{dt^4} + (L_1^2 S C^2 + 2 L_1 L_2 C^2 G) \frac{d^3}{dt^3} + (2 L_1 C^2 G S + L_2 G^2 C^2) \frac{d^2}{dt^2} \right.$$
$$\left. + (\overline{G+S} C L_1 + C^2 G^2 S) \frac{d}{dt} + G C \overline{G+S} \right)^{-1} 0.$$

This linear differential equation is solved when we know the roots of the auxiliary biquadratic; and according as they are all real or partly imaginary, so will be the nature of the solution.

If the roots are all real the solution is a sum of exponentials, whose total value first increases and then dies away as t increases, indicating that the discharge produces a wave of electricity through the galvanometer always in one direction; but if two or all of the roots of the auxiliary biquadratic are unreal, it indicates as the form of solution a function of sines and cosines which will have periodic values, and points to the fact that the discharge is a series of alternations. The general case, when both the galvanometer and shunt have coefficients of self-induction, when treated to determine the conditions for an oscillating discharge, leads to an expression of considerable complexity and not much practical use. The reduced case, in which the galvanometer is wound to have self-induction and the shunt so as to have no coefficient of self-induction, is, however, a practical case, and can be treated without much difficulty.

Taking the differential equation for q, equation (iv.), and writing in it $L_2 = 0$, we have

$$CL_1 S \frac{d^2 q}{dt^2} + CGS \frac{dq}{dt} + (G+S) q = 0,$$

or

$$\frac{S}{G+S} \frac{d^2 q}{dt^2} + \frac{GS}{L_1(G+S)} \frac{dq}{dt} + \frac{q}{CL_1} = 0.$$

The discharge will be oscillatory if the auxiliary quadratic

$$\frac{S}{G+S} m^2 + \frac{GS}{L_1(G+S)} m + \frac{1}{CL_1} = 0$$

has unreal or imaginary roots.

Solving it we have

$$m^2 + \frac{Gm}{L_1} + \frac{G^2}{4L_1{}^2} = \frac{G^2}{4L_1{}^2} - \frac{G+S}{SCL_1},$$

or

$$\left(m + \frac{G}{2L_1}\right) = \pm \frac{\sqrt{G^2S^2C^2 - 4\overline{G+S}\,L_1SC}}{2L_1SC.}$$

Hence, for the roots to be imaginary,

$$4L_1 \,\overline{G+S}\,SC \text{ must be greater than } G^2S^2C^2,$$

or

$$\frac{4L^1}{C} > \frac{G \cdot GS}{G+S}.$$

If this relation holds good, then the discharge is oscillatory in the condenser; and accordingly we see that to prevent electrical oscillation in the galvanometer circuit, the product of resistance of the galvanometer and combined resistance of galvanometer and shunt must be equal to or greater than four times the self-induction of the galvanometer divided by the capacity of the condenser.

We may write the solution of the quadratic above,

$$m = -\frac{G}{2L_1} \pm \sqrt{-1} \sqrt{\frac{\frac{G+S}{S}}{L_1C} - \frac{G^2}{4L_1^2}}$$

$$= -a \pm \sqrt{-1}\,\beta,$$

where

$$a = \frac{G}{2L_1} \quad \text{and} \quad \beta = \sqrt{\frac{\frac{G+S}{S}}{L_1C} - \frac{G^2}{4L_1^2}};$$

and accordingly when β is real, that is when

$$\frac{\frac{G+S}{S}}{L_1C} \text{ is } > \frac{G^2}{4L_1^2},$$

we have, for solution of equation,

$$q = Ae^{-at}\cos \beta t + Be^{-at}\sin \beta t.$$

When $t=0$, $q=Q=$ the original charge of the condenser, and $\frac{dq}{dt}=0$ when $t=0$;

therefore

$$Q=A \quad \text{and} \quad Q\frac{a}{\beta}=B;$$

and

$$q = Qe^{-at}\left(\cos \beta t + \frac{a}{\beta}\sin \beta t\right).$$

Having now the value of the quantity of electricity left in the condenser at any instant, we can find easily, from the cycle equation (i.), the value of the current through the galvanometer. For

$$L_1\frac{dy}{dt} + Gy = \frac{q}{C},$$

or

$$\frac{dy}{dt} + \frac{G}{L}y = \frac{q}{CL};$$

$$\therefore\ \ y=e^{-\int\frac{G}{L}dt}\left\{C'+\int e^{\int\frac{G}{L}dt}\frac{q}{CL}\,dt\right\},$$

and the constant C' is determined by the condition $y=0$ when $t=0$.

Substituting the value of q above, we have

$$a=\frac{G}{2L},$$

$$y=e^{-2at}\left\{C'+\frac{1}{\beta}\frac{Q}{CL}\int e^{at}(\beta\cos\beta t+a\sin\beta t)\right\}$$

$$=e^{-2at}\left\{C'+\frac{Q}{\beta CL}e^{at}\sin\beta t\right\};$$

but $C'=0$,

$$\therefore\ \ y=\frac{Q}{\beta CL_1}e^{-at}\sin\beta t;$$

and since

$$a=\frac{G}{2L_1}\ \ \text{and}\ \ \beta=\sqrt{\frac{\frac{G+S}{S}}{L_1C}-\frac{G^2}{4L_1^2}},$$

$$y=\frac{Q}{\sqrt{\frac{G+S}{S}CL_1-\frac{G^2C^2}{4}}}e^{-\frac{G}{2L_1}t}\sin\left(\sqrt{\frac{G+S}{SL_1C}-\frac{G^2}{4L_1^2}}\right)t,$$

which gives the value of the instantaneous current in the galvanometer-circuit at any instant t after starting a discharge from a condenser of capacity C and original quantity Q through a shunted galvanometer, the shunt being wound without self-induction, and the galvanometer having a coefficient of self-induction L_1.

§ 19. Two concluding examples of this method of treating network problems will now be given, which are in Professor Clerk Maxwell's own words*.

* In the May term 1879, Professor Clerk Maxwell lectured at Cambridge on Electromagnetism, and in the two last lectures of the Course he

Theorem.—To compare the induction between one pair of coils and any other two.

Let a, β, γ, δ be four coils of wire.

It is required to compare the mutual induction of a and γ with that of β and δ.

Join up a and β coils in series with a galvanometer, and join up γ and δ coils in multiple arc with a battery, as shown in fig. 18.

Place the coils in position.

Let S and R be resistances of the primaries γ and δ; let θ be resistance of the two secondaries and of the galvanometer.

Let L_1, L_2, N_1, N_2 be the coefficients of self-induction of the coils, and M_1, M_2 the coefficients of mutual induction of a and γ, β and δ. Let Γ be the coefficient of self-induction of the galvanometer.

Call x the cycle current of γ, y that of δ, and z that of the circuit formed of a, β, and the galvanometer.

The kinetic energy T of the system is

$$2\mathrm{T} = x^2 \mathrm{N}_1 + xz\mathrm{M}_1 + z^2(\mathrm{L}_1 + \mathrm{L}_2 + \Gamma) + y^2 \mathrm{N}_2 + 2yz\mathrm{M}_2,$$

and the dissipation function F is

$$2\mathrm{F} = x^2 \mathrm{R} + y^2 \mathrm{S} + z^2 \mathrm{Q}.$$

Then, by the formula

$$\mathrm{E} = \frac{d}{dt}\frac{d\mathrm{T}}{dx} + \tfrac{1}{2}\frac{d\mathrm{F}}{dx},$$

$$\dot{x}\mathrm{N}_1 + \dot{z}\mathrm{M}_1 + x\mathrm{R} = \mathrm{E}.$$

$$\dot{y}\mathrm{N}_2 + \dot{z}\mathrm{M}_2 + y\mathrm{S} = -\mathrm{E}.$$

$$\dot{x}\mathrm{M}_1 + \dot{y}\mathrm{M}_2 - \dot{z}(\mathrm{L}_1 + \mathrm{L}_2 + \Gamma) + 2\mathrm{Q} = 0.$$

Now $x-y$ is the current through the battery; hence if we put $x+y$ for x in the above, we shall get x as the battery-current. Hence, making the change, we have

---

gave this method of obtaining the equation for the currents in a network of conduction. In the last lecture of all he applied the method to cases in which self and mutual induction was taken into account, and gave the two illustrations in § 19. At the conclusion of this lecture he had ended his professorial duties for the term, and a melancholy interest attaches to the subject which occupied his mind on the last occasion on which, unconsciously to himself or his pupils, he was to perform them. Those who enjoyed even for a brief period the privilege of being taught by him, ever cherish a vivid remembrance of the intellectual treat afforded by Professor Maxwell's lecture-teaching, and the profound suggestiveness and interest of it.

The two examples in § 19 and § 20 are taken from my notes of Prof. Maxwell's lectures, with some little alterations to make them clearer.

$$(\dot{x}+\dot{y})\mathrm{N}_1 + \dot{z}\mathrm{M}_1 + \overline{\dot{x}+\dot{y}}\mathrm{R}=\mathrm{E}, \quad . \quad . \quad . \quad . \quad . \text{(i.)}$$

$$\dot{y}\mathrm{N}_2 \qquad + \dot{z}\mathrm{M}_2 + y\mathrm{S}=-\mathrm{E}, \quad . \quad . \quad . \quad . \quad . \quad . \text{(ii.)}$$

$$(x+\dot{y})\mathrm{M}_1 + \dot{y}_1\mathrm{M}_2 - \dot{z}(\mathrm{L}_1+\mathrm{L}_2+\Gamma)+2\mathrm{Q}=0; \quad . \text{(iii.)}$$

add equations (i.) and (ii.) and arrange, putting n for $\dfrac{d}{dt}$,

$$(\mathrm{N}_1 n + \mathrm{R})x + (\mathrm{N}_1 n + \mathrm{N}_2 n + \mathrm{R} + \mathrm{S})y + (\mathrm{M}_1 + \mathrm{M}_2)nz = 0,$$

$$\mathrm{M}nx + (\mathrm{M}_1 n + \mathrm{M}_2 n)y + \{(\mathrm{L}_1 + \mathrm{L}_2 + \Gamma)n + \mathrm{Q}\}z = 0.$$

Eliminating y, we have

$$\{n(\mathrm{N}_1 n + \mathrm{R})(\mathrm{M}_1 + \mathrm{M}_2) - \mathrm{M}_1 n(\mathrm{N}_1 n + \mathrm{N}_2 n + \mathrm{R} + \mathrm{S})\}x$$

$$+ ((\mathrm{M}_1 + \mathrm{M}_2)^2 n^2 - \{(\mathrm{L}_1 + \mathrm{L}_2 + \Gamma)n + \mathrm{Q}\} \{\mathrm{N}_1 n + \mathrm{N}_2 n + \mathrm{R} + \mathrm{S}\})z = 0.$$

Hence we get

$$z = \frac{\{n^2(\mathrm{M}_2\mathrm{N}_1 - \mathrm{M}_1\mathrm{N}_2) - n(\mathrm{M}_1\mathrm{S} - \mathrm{M}_2\mathrm{R})\}\,x}{\text{a denominator which does not concern us}}.$$

If matters are so arranged that $z=0$, or the galvanometer shows no current,

$$(\mathrm{M}_2\mathrm{N}_1 - \mathrm{M}_1\mathrm{N}_2)\frac{dx}{dt} = (\mathrm{M}_1\mathrm{S} - \mathrm{M}_2\mathrm{R});$$

hence if there is no " kick." on the galvanometer on making the current, then

$$\frac{\mathrm{M}_1}{\mathrm{M}_2} = \frac{\mathrm{R}}{\mathrm{S}}.$$

§ 20. *Theorem.*—To determine the capacity of a condenser by means of a Wheatstone's bridge (fig. 19).

Let α, β, γ, δ be the four points of a Wheatstone's bridge; and let the branch between α and β be interrupted at $a\,b$, and a Leyden jar or condenser inserted provided with some rapid commutator, such as a tuning-fork, so that whilst the outside of the jar is kept permanently attached to β, the inside is alternately joined to a and b.

If a tuning-fork is used and its prongs have small metal styles which just come down to the surface of the mercury in two little cups, when the fork vibrates, as the prongs come together, the upper point dips in; and as they separate, the lower one dips in; hence the shank of the fork is alternately connected with one and the other cup. The interval between the time of connection being exactly half the time of a complete oscillation of the fork.

Now let the meshes of the network be called $x+z$, z, and y;

then x is the current through the galvanometer, and y is the current through the battery. When the arrangement is made as in the diagram, and the fork set vibrating, the vibrating fork and the condenser act together like a resistance, and let through so much electricity per second.

Now, as the condenser gets its charge by electricity flowing into it, it builds up an opposing electromotive force in the z circuit which at any instant is equal to the value of $\dfrac{\int z\,dt}{K}$, where K is the capacity of the jar, the integral being integrated from the instant when the charging commences up to the instant considered. Now, if the fork makes n vibrations a second when the steady state is set up, the current z which flows into the jar has a mean value z; and therefore $\dfrac{z}{nK}$ is the opposing electromotive force in that branch.

Accordingly, the condenser and associated commutator behave like a voltameter inserted in the branch $\alpha\beta$, or like a resistance with a counter electromotive force in it. Only such a combined jar and fork differs from an ordinary metallic resistance in this, that its apparent resistance is not constant, but depends on two things, the speed of commutation or charge and recharge, and the capacity of the condenser; whilst the counter electromotive force depends on the current z, and, being represented by $\dfrac{z}{nK}$, is dependent not only on n and K, but also on the values of all the other resistances in the branches. In the first place, we require an expression for the electromotive force charging the condenser. Let the difference of potential between a and b be called e. Then consider the network formed by the five conductors R, S, Q, G, and B with the electromotive force in the branch B; write down the network equations for this z mesh network.

$$(B + R + S)y - S(x + z) = E,$$
$$-Sy + (Q + S + G)(x + z) = 0.$$

Hence

$$y = \frac{E(Q + S + G)}{\delta};$$

and

$$x + z = \frac{ES}{\delta},$$

where $\delta =$ the determinant

$$\begin{vmatrix} B + R + S, & -S \\ -S, & Q + S + G \end{vmatrix}$$

T 2

which is
$$S(Q+G)+(R+B)(Q+S+G).$$

Now the difference of potential e between a and b when the condenser is just beginning to be charged is
$$G(x+z)+Ry=e;$$
$$\therefore\ e=\frac{ESG}{\delta}+\frac{ER(Q+S+G)}{\delta}$$

$$=E\frac{SG+R(Q+S+G)}{S(Q+G)+(R+B)(Q+S+G)}=\frac{\begin{vmatrix}-G, & -R \\ Q+S+G, & -S\end{vmatrix}}{S(Q+G)+(R+B)(Q+S+}$$

or
$$e=E\frac{\begin{vmatrix}-G, & -R \\ Q+S+G, & -S\end{vmatrix}}{\delta}.$$

Now if the electromotive force e be employed n times in a second to charge a jar of capacity K, the average current flowing into the jar is $nKe=z$.

Now to find z we have to consider the distribution of currents when the fork or commutator is in operation, and the condenser allowing a flow of electricity to take place through it.

Let P be the resistance which could equivalently replace the jar and fork—that is, would allow an equal quantity of electricity to pass per second; then, since $\frac{z}{nK}$ is the opposing electromotive force in this branch, we have the following equation for the three cycles x, $x+z$, and y:—

$$-Sx+(R+S+B)y-(R+S)z=E,$$
$$-Gx-Ry+(P+R)z=-\frac{z}{nK},$$
$$(Q+S+G)x-Sy+(Q+S)z=0.$$

Now let Δ stand for the determinant
$$\begin{vmatrix}-S, & R+S+B, & -(R+S) \\ -G, & -R, & P+\dfrac{1}{nK}+R \\ Q+S+G, & -S, & Q+S\end{vmatrix}.$$

Then the solution of the above equations for z and x are
$$z=\frac{E\begin{vmatrix}-G, & -R \\ Q+S+G, & -S\end{vmatrix}}{\Delta},$$

and

$$x = \frac{E \begin{vmatrix} -R, & P + \dfrac{1}{nK} + R \\ -S, & Q + S \end{vmatrix}}{\Delta}.$$

z is the average current flowing through the condenser, and x is the current through the galvanometer. Now let the resistances R, S, and Q be so varied that the current through the galvanometer is zero, then $x = 0$; and therefore

$$\begin{vmatrix} -R, & P + \dfrac{1}{nK} + R \\ -S, & Q + S \end{vmatrix} = 0,$$

or

$$R(Q + S) = S\left(P + \frac{1}{nK} + R\right),$$

or

$$\frac{RQ}{S} = P + \frac{1}{nK}.$$

Now insert this value for $P + \dfrac{1}{nK}$ in the determinant Δ above and calculate its value, and we arrive at the expression

$$\Delta = \frac{\{B(Q + S) + Q(R + S)\}\{G(R + S) + R(Q + S)\}}{S}.$$

We have now, by substitution of this value of Δ in the value obtained above for z, an expression for the value of the average current through the condenser when the bridge is balanced, and it is

$$z = \frac{ES \begin{vmatrix} -G, & -R \\ Q + S + G, & -S \end{vmatrix}}{\{B(Q + S) + Q(R + S)\}\{G(R + S) + R(Q + S)\}}.$$

Equating this to the other value for z, namely,

$$z = nKe = nKE \frac{\begin{vmatrix} -G, & -R \\ Q + S + G, & -S \end{vmatrix}}{S(Q + G) + (R + B)\{Q + S + G\}},$$

we have

$$nK = \frac{S\{S(Q + G) + (R + B)(Q + S + G)\}}{\{B(Q + S) + Q(R + S)\}\{G(R + S) + R(Q + S)\}},$$

which gives us a value for nK in terms of
$$B, Q, R, S, G.$$

Now it is interesting to note that we may otherwise write the above expression for nK,

$$\frac{1}{n\mathrm{K}} = \frac{\Delta}{\delta},$$

where Δ is the determinant,

$$\begin{vmatrix} \mathrm{R+B+S}, & -\mathrm{S}, & -\overline{\mathrm{R+S}} \\ -\mathrm{S}, & \mathrm{Q+S+G}, & \mathrm{R}\left(\dfrac{\mathrm{Q}}{\mathrm{S}}+1\right) \\ -\mathrm{R}, & -\mathrm{G}, & \mathrm{Q+S} \end{vmatrix},$$

and δ is its first minor,

$$\begin{vmatrix} \mathrm{R+B+S}, & -\mathrm{S} \\ -\mathrm{S}, & \mathrm{Q+S+G} \end{vmatrix},$$

and $\dfrac{1}{n\mathrm{K}}$ is of the dimensions of a resistance.

The value for nK writes out by a simple transformation into another form,

$$n\mathrm{K} = \frac{\mathrm{S}\left\{1 - \dfrac{\mathrm{S}^2}{(\mathrm{Q+S+G})(\mathrm{R+B+S})}\right\}}{\mathrm{RQ}\left\{1 + \dfrac{\mathrm{SB}}{\mathrm{Q(R+B+S)}}\right\}\left\{1 + \dfrac{\mathrm{SG}}{\mathrm{R(Q+S+G)}}\right\}};$$

which is the form in which it is given by Prof. J. J. Thomson in his paper, and quoted by Mr. R. T. Glazebrook in his memoir on a Method of Measuring the Capacity of a Condenser*.

The above examples are amply sufficient to exemplify this method of treating problems in networks of conductors, and show how it enables calculations to be made with considerable ease, not only of the distribution of currents and potentials, but of the resistances between any points on a network, the branches of which consist either of simple resistances or of wires having self- and mutual induction with other branches, or of electromagnets, or condensers associated with appropriate commutators.

* This method of Maxwell's, of obtaining the capacity of a condenser has been practically employed, with most excellent results, by Mr. R. T. Glazebrook, F.R.S. ; and the full details of the tests to which he subjected the method are given in his paper in the 'Proceedings of the Physical Society,' vol. vi. part iii. p. 204 (June 28, 1884). [Phil. Mag. for August 1884, p. 98.]

XXVIII. *The Periodic Law, as Illustrated by certain Physical Properties of Organic Compounds.*—Part I. *The Alkyl Compounds of the Elements. By* Thomas Carnelley, *D.Sc., Professor of Chemistry in University College, Dundee*[*].

IN a previous communication (Phil. Mag. [5] xviii. p. 1) I have shown how the truth of the Periodic Law may be illustrated by means of the melting- and boiling-points and heats of formation of the normal halogen compounds of the elements. I shall now endeavour to show how the same law is further confirmed in a similar manner by the physical properties of certain compounds of Organic Chemistry. For this purpose we shall make use of the normal alkyl compounds (methides, ethides, propides, &c.) of the elements; and in the sequel we shall find that exactly the same relations hold good with these compounds as in the case of the corresponding chlorides, bromides, and iodides.

As the melting-points and heats of formation of but very few of these compounds have been determined, we shall necessarily be limited to a consideration of the boiling-points and specific gravities.

As pointed out by Mendeljeff (*Ann. Chem. Pharm.* Suppl. 1872, p. 151), elements belonging to even series (except series 2) do not combine with alcohol radicals to form methides, ethides, &c., whilst those belonging to odd series generally do so combine. In what follows, therefore, we shall merely be able to take into consideration elements belonging to odd series and to the first even series only.

Table I. contains the experimental data, with the authorities, on which our conclusions are based. For the purpose of avoiding minus signs, all temperatures are reckoned from the absolute zero ($-273°$). The specific gravities employed were those corresponding as nearly as possible to $15°$ C.; but it was not possible to take them all at a uniform temperature throughout, as in many instances there is only one determination on record, and that was made at different temperatures in the several cases; whilst scarcely any of them have been determined at, or equally distant from, the boiling-point. The following abbreviations are employed :—Me = methyl, CH_3; Et = ethyl, C_2H_5; Pr = normal propyl, C_3H_7; Bu = normal butyl, C_4H_9; Ph = phenyl, C_6H_5.

* Communicated by the Author.

TABLE I.

	Boiling-point.	Authority.	Specific gravity.	Authority.
BMe_3	b. 257	Frankland.		
CMe_4	282	Lwow.		
NMe_3	281	Vincent.		
OMe_2	249	Regnault.		
$AlMe_3$......	403	Buckton and Odling.		
$SiMe_4$	303	Friedel and Crafts.		
PMe_3	314	Hofmann and Cahours.		
SMe_2	314	Regnault.	·845 (21)	Regnault.
$ClMe$	249	,,		
$ZnMe_2$ ...	319	Frankland and Duppa.	1·386 (11)	Frankland and Duppa.
$AsMe_3$ ...	b. 373	Cahours.		
SMe_2 ...	331	Jackson.		
$BrMe$ ...	277	Perkin.	1·664 (0)	Pierre.
$SnMe_4$ ...	351 *	Ladenburg.	1·314 (0)	Ladenburg.
$SbMe_3$ ...	354	Landolt.	1·523 (15)	Landolt.
$TeMe_2$ ...	355	Wöhler and Dean.		
IMe	317	Haagen.	2·264	Haagen.
$HgMe_2$ ...	367	Buckton.	3·069	Buckton.
$PbMe_4$ ...	433 †	Cahours.	2·034 (0)	Butlerow.
$BeEt_2$ ...	459	,,		
BEt_3	369	Frankland and Duppa.	·696	Frankland and Duppa.
NEt_3	362	Brühl.	·728 (20)	Brühl.
OEt_2	308	Kopp.	·735 (0)	Kopp.
FEt	283(?)	Landolph.		
$AlEt_3$	467	Buckton and Odling.		
$SiEt_4$	425	Friedel and Crafts.	·766 (23)	Friedel and Crafts.
PEt_3	401	Hofmann and Cahours.	·812 (15)	Hofmann and Cahours.
SEt_2	364	Pierre.	·837 (0)	Pierre.
$ClEt$	285	Linnemann.	·925 (0)	Linnemann.
$ZnEt_2$......	391	Frankland.	1·182 (18)	Frankland.
$AsEt_3$ ... {	413–453 say 432	Landolt.	1·151 (17)	Landolt.
$SeEt_2$	381	Pieverling.		
$BrEt$	312	Linnemann.	1·468 (13)	Linnemann.
$SnEt_4$	454	Frankland.	1·187 (14)	Frankland.
$SbEt_3$	432	Löwig.	1·324 (16)	Löwig.
$TeEt_2$	b. 373	Wöhler.		
IEt.........	345	Linnemann.	1·944 (15)	Linnemann.
$HgEt_2$ ...	432	Buckton.	2·444	Buckton.
$PbEt_4$ ...	473	Buckton.	1·585	,,
$BiEt_3$	......	......	1·820	Breed.

* 413 Cahours.   † 373 Butlerow.

Table I. (*continued*).

	Boiling-point.	Authority.	Specific gravity.	Authority.
BePr$_2$......	518	Cahours.		
NPr$_3$	429	Zander.		
OPr$_2$	357	Linnemann.		
AlPr$_3$	523	Cahours.		
SiPr$_4$	486	Pape.	·762 (15)	Pape.
SPr$_2$	405	Cahours.	·814 (17)	Cahours.
ClPr	319	Linnemann.	·896 (19)	Linnemann.
ZnPr$_2$	432	Cahours.	1·098 (15) {	Gladstone and Tribe.
BrPr	344	Rossi.	1·388 (0)	Rossi.
SnPr$_4$......	498	Cahours.	1·179	Cahours.
IPr.........	375	Linnemann.	1·747 (16)	Linnemann.
HgPr$_2$ ...	464	Cahours.	2·124 (16)	Cahours.
NBu$_3$	486	{ Lieben and Rossi. }	·778 (20) {	Lieben and Rossi.
OBu$_2$	413	,,	·768 (20)	,,
SBu$_2$	455	Grabowsky.	·839 (16)	Grabowsky.
ClBu	351	Linnemann.	·887 (20) {	Lieben and Rossi.
ZnBu$_2$ ...	461	Cahours.		
BrBu	373	Linnemann.	1·299 (20)	Linnemann.
IBu	403	,,	1·580 (18)	,,
HgBu$_2$ ...	479	Cahours.	1·835 (15)	Cahours.
CPh$_4$ ... {	m.p. 218	Behr.		
	b.p. a. 633	Friedel and Crafts.		
NPh$_3$ ... {	m.p. 400	Merz and Weith.		
	b.p. a. 573			
OPh$_2$ ... {	m.p. 301	} Hoffmeister.		
	b.p. 519			
FPh ... {	m.p. b. 253	} Paternò and Oliveri.		
	b.p. 358			
SiPh$_4$ ... {	m.p. 501	} Polis.		
	b.p. a. 633			
SPh$_2$	b.p. 565	Stenhouse.	1·119	Stenhouse.
ClPh ... {	m.p. 233	} Jungfleisch.	1·219 (0)	Jungfleisch.
	b.p. 404			
AsPh$_3$... {	m.p. 331	} La Coste and Michaelis.		
	b.p. 633			
BrPh ... {	m.p. b. 253	} Adrienz.	1·502 (12)	Adrienz.
	b.p. 427			
IPh ... {	m.p. b. 255	Schutzenberger. Kekulé.	} 1·640 (15)	Ladenburg.
	b.p. 461			
HgPh$_2$ {	m.p. 393	} Dreher and Otto.		
	b.p. a. 573			

RELATION 1. (a) *If the elements be arranged in the order of their atomic weights, then the boiling-points of their alkyl compounds rise and fall periodically.* (b) *Under similar conditions, the specific gravities diminish up to the middle member and then increase to the last member of each series.* (See Table II.)

The exceptions to this rule, in the case of the boiling-points, occur either at or near the maxima or minima (*i. e.* at the

turning-points) of Meyer's curve of the elements (*Mod. Theor. der Chem.*), in which respect they resemble those corresponding halogen compounds of the elements which are exceptions to the same rule.

The above facts are shown in the following Table :—

TABLE II.—Illustrating Relations 1 and 2.

	METHIDES.		ETHIDES.		α-PROPIDES.		α-BUTIDES.		PHENIDES*.		
	B.P.	Sp. gr.	B.P.	Sp. gr.	B.P.	Sp. gr.	B.P.	Sp. gr.	M.P.	B.P.	Sp. gr.
Li ...											
Be ...	......	......	459	......	518						
B......	b. 257	......	369	·696							
C......	282	......	......	......	......	......	......	......	418	a. 633	
N......	281	......	362	·728	429	......	486	·778	400	a. 573	
O......	249	......	308	·735	357	......	413	·768	301	519	
F......	......	......	283	......	......	......	......	.....	b. 253	358	
Na ...											
Mg ...											
Al ...	403	......	467	......	523						
Si ...	303	......	425	·766	486	·762	......	......	501	633	
P......	314	......	401	·812							
S......	310	·845	364	·837	405	·814	455	·839	......	565	1·119
Cl ...	249	......	285	·925	319	·896	351	·887	233	404	1·129
Cu ...											
Zn ...	319	1·386	391	1·182	432	1·098	461				
Ga ...											
Eka-Si											
As ...	b. 373	......	432	1·151	......	......	......	......	331	633	
Se ...	331	......	381								
Br ...	277	1·664	312	1·468	344	1·388	373	1·299	b. 253	427	1·502
Ag ...											
Cd ...											
In ...											
Sn ...	351	1·314	454	1·187	498	1·179					
Sb ...	354	1·523	432	1·324							
Te ...	355	......	b. 373								
I	317	2·264	345	1·944	375	1·747	403	1·580	b. 255	461	1·640
Au ...											
Hg ...	367	3·069	432	2·444	464	2·124	479	1·835	393	a. 573	
Tl ...											
Pb ...	433	2·034	473	1·535							
Bi ...	......	......	......	1·820							

* The phenides of course are not comparable with the methides, ethides, &c., though they appear to obey the same rules.

RELATION 2. *The boiling-point increases and the specific gravity diminishes as we pass from the methide to the ethide and thence to the propide, butide, &c.* (See Tables II. and III.)

RELATION 3. *The boiling-points and specific gravities of the alkyl compounds of any one group increase as the atomic weight of the positive element increases.* (See Table III.)

TABLE III.—Illustrating Relations 2 and 3.

	METHIDES.		ETHIDES.		α-PROPIDES.		α-BUTIDES.		PHENIDES.		
	B.P.	Sp. gr.	B.P.	Sp. gr.	B.P.	Sp. gr.	B.P.	Sp. gr.	M.P.	B.P.	Sp. gr.
Cl ...	249	......	285	·925	319	·896	351	·887	233	404	1·129
Br ...	277	1·664	312	1·468	344	1·388	373	1·299	b. 253	427	1·502
I	317	2·264	345	1·944	375	1·747	403	1·580	b. 255	461	1·640
Si......	303	......	425	·766	486	·762	......	......	501	633	
Sn ...	351	1·314	454	1·187	498	1·179					
Pb ...	433	2·034	473	1·585							
Zn ...	319	1·386	391	1·182	432	1·098	461				
Hg ...	367	3·069	432	2·444	464	2·124	479	1·835	393	a. 573	
P......	314	......	401	·812							
As ...	b. 373	......	432	1·151							
Sb ...	354	1·523	432	1·324							
Bi ...	......	......	......	1·820							
S......	310	·845	364	·837							
Se ...	331	......	381								
Te ...	355	......	b. 373(?)								

RELATION 4. *The differences between the boiling-points (and also between the specific gravities) of the methides and ethides, of the ethides and propides, of the propides and butides, &c., increase algebraically from the beginning of each series up to the fourth or middle (tetrad) member and then diminish to the seventh or last member.* (See Table IV., which gives the available data for the Second Series.)

TABLE IV.—Diff. of Boiling-points. Illustrating Relation 4.

	Ethide minus Methide.	Propide minus Ethide.	Butide minus Propide.	Propide minus Methide.	Butide minus Ethide.	Butide minus Methide
Diff. in atomic weight of alkyl radicals....	....	14		28		42
Na						
Mg						
Al	65	56	......	120		
Si	122	61	......	183		
P	87	...	......	......		
S	54	41	50	95	91	145
Cl	36	34	32	70	66	102

RELATION 5. *The differences referred to in (4) increase* on the average *in nearly the same proportion as the difference between the atomic weights of the alkyl radicals* (see Table V.) ; *whilst in the case where the difference between the atomic weights of the alkyl radicals is the same, the difference between the boiling-points either tends to become equal, or diminishes as the atomic weights of the alkyl radicals increase* (see Table IV.; also compare Kopp's Law of the Boiling-points of Homologous Series).

TABLE V.—Illustrating part of Relation 5.

Formula	$X =$ Difference in atomic weights of alkyl radicals.	Cl. — Calculated.	Cl. — Experimental mean.	Br. — Calculated.	Br. — Experimental mean.	I. — Calculated.	I. — Experimental mean.
$X\,C_{n+1}H_{2n+3} - X\,C_n H_{2n+1}$	$14\times1=14$	**Cl.** $34\times1=34$	34	**Br.** $32\times1=32$	33	**I.** $29\times1=29$	29
$X\,C_{n+2}H_{2n+5} - X\,C_n H_{2n+1}$	$14\times2=28$	$34\times2=68$	68	$32\times2=64$	64	$29\times2=58$	58
$X\,C_{n+3}H_{2n+7} - X\,C_n H_{2n+1}$	$14\times3=42$	$34\times3=102$	102	$32\times3=96$	96	$29\times3=87$	87
$X(C_{n+1}H_{2n+3})_2 - X(C_n H_{2n+1})_2$	$14\times1=14$	**O.** $54\times1=54$	54	**S.** $47\times1=47$	45	**Zn.** $47\times1=47$	47
$X(C_{n+2}H_{2n+5})_2 - X(C_n H_{2n+1})_2$	$14\times2=28$	$54\times2=108$	107	$47\times2=94$	93	$47\times2=94$	92
$X(C_{n+3}H_{2n+7})_2 - X(C_n H_{2n+1})_2$	$14\times3=42$	$54\times3=162$	164	$47\times3=141$	145	$47\times3=141$	142
$X(C_{n+1}H_{2n+3})_3 - X(C_n H_{2n+1})_3$	$14\times1=14$	**N.** $68\times1=68$	68	**Al.** $60\times1=60$	60		
$X(C_{n+2}H_{2n+5})_3 - X(C_n H_{2n+1})_3$	$14\times2=28$	$68\times2=136$	136	$60\times2=120$	120		
$X(C_{n+3}H_{2n+7})_3 - X(C_n H_{2n+1})_3$	$14\times3=42$	$68\times3=204$	205				
$X(C_{n+1}H_{2n+3})_4 - X(C\ O\ H_{2n+1})_4$	$14\times1=14$	**Si.** $91.5\times1=91.5$	91.5	**Sn.** $73.5\times1=73.5$	73.5		
$X(C_{n+2}H_{2n+5})_4 - X(C_n H_{2n+1})_4$	$14\times2=28$	$91.5\times2=183$	183	$73.5\times2=147$	147		
$X(C_{n+3}H_{2n+7})_4 - X(C_n H_{2n+1})_4$	$14\times3=42$						

RELATION 6. *The differences referred to in* (4), *for both boiling-points and specific gravities, diminish algebraically as the atomic weight of the positive element increases.* (See Table VI.)

TABLE VI.—Illustrating Relation 6.

Diff. in at. wts. of alkyl radicals.	14						28				42	
	$C_2H_5-CH_3$.		$C_3H_7-C_2H_5$.		$C_4H_9-C_3H_7$		$C_3H_7-CH_3$.		$C_4H_9-C_2H_5$		$C_4H_9-CH_3$.	
	B.P.	Sp. gr.	B.P.	Sp. gr.	B.P.	Sp. gr.	B.P.	Sp. gr,	B.P.	Sp. gr.	B.P.	Sp. gr.
Cl	36	......	34	−·029	32	−·009	70	......	66	−·038	102	
Br	35	−·196	32	−·080	29	−·089	67	−·276	61	−·169	96	−·365
I	28	−·320	30	−·197	28	−·167	58	−·517	58	−·364	86	−·684
Si	122	......	61	−·004	......	......	183					
Sn	103	−·127	44	−·008	......	......	147	−·135				
Pb	40	−·449										
Zn	72	−·204	41	−·084	29	......	113	−·288	70	......	142	
Hg	65	−·625	32	−·320	15	−·289	97	−·945	47	−·609	112	−1·234

	$C_2H_5-CH_3$.			$C_2H_5-CH_3$.	
	B.P.	Sp. gr.		B.P.	Sp. gr.
S	54	−·008	P......	87	
Se	50		As ...	a. 59	
Te	18		Sb ...	78	−·199

RELATION 7. (a) *The differences between the boiling-points, and also between the specific gravities, of the methides, or ethides, or propides, or butides, &c. of the elements of the same group diminish as we pass from the methides to the ethides and thence to the propides, &c.*

(b) *The above differences, as regards the boiling-points, increase as the difference between the atomic weights of the two positive elements increases.* (See Table VII.)

TABLE VII.—Illustrating Relation 7.

I.	Diff. of atomic weights of elements in I.	METHIDES.		ETHIDES.		PROPIDES.		BUTIDES.		PHENIDES.	
		B.P.	Sp. gr.	B.P.	Sp. gr.	B.P.	Sp. gr.	B.P.	Sp. gr.	B.P.	Sp. gr.
Br–Cl ...	44·5	28	......	27	·543	25	·492	22	·412	23	·373
I–Br ...	47·0	40	·600	33	·476	31	·359	30	·281	34	·138
I–Cl ...	91·5	68	......	60	......	56	......	52	......	57	
Pb–Sn...	89	82(?)	·720	19	·398						
Sn–Si ...	90	48	......	29	·421	12	·417				
Pb–Si ...	179	130	... ..	48	·784						
Hg–Zn ..	135	48	1·683	41	1·262	32	1·026	18			

RELATION 8. (a) *The differences between the boiling-points (and also between the specific gravities) of the methides, ethides, propides, &c. of the elements of the seventh or halogen group and those of the elements of groups* iii. *to* vii. *respectively increase algebraically from the methides to the ethides, and thence to the propides &c.* (See Table VIII.)

(b) *With members of the second group* (Zn, Hg, &c.) *these differences as regards the specific gravities diminish algebraically from methides to butides.* (See Table VIII.) Whilst as regards the boiling-points of the second group, the first part of the rule (a) seems to hold good, except in so far as a tendency to a reversal of the rule appears as we approach the butides and higher alkyl compounds ; and this reversal becomes the more pronounced the greater the difference in the atomic weights of the metal and the halogen. Data are entirely wanting for the first group.

RELATION 9. *The differences referred to in Relation 8, for both boiling-points and specific gravities, increase algebraically as the algebraic difference between the atomic weights of the positive elements increases.* (See Table VIII.)

TABLE VIII.—Illustrating Relations 8 and 9.

I.	Diff. of atomic weights of elements in I.	METHIDES.		ETHIDES.		PROPIDES.		BUTIDES.		PHENIDES.	
		B.P.	Sp. gr.	B.P.	Sp. gr.	B.P.	Sp. gr.	B.P.	Sp. gr.	B.P.	Sp. gr.
S–I......	−95	− 7	−1·419	+19	−1·107	+30	−·933	+52	−·741	+104	−·521
Se–I ...	−48	+14	......	36							
S–Br...	−44·5	33	−·819	52	− ·631	61	−·574	82	−·460	138	−·383
S–Cl ...	− 3·5	61	......	79	− ·088	86	−·082	104	−·048	161	−·010
Te–I ...	− 2	38	......	28?							
Se–Br...	− 1	54	......	69							
Se–Cl ...	+43·5	82	......	96							
Te–Br...	45	78	......	61?							
Te–Cl...	89·5	106	......	88?							
P–I......	−96	− 3	......	+56	−1·132	......	......	......	......	172	
As–I ...	−52	b. +56	......	87	− ·793						
P–Br ...	−49	37	......	89	− ·656						
Sb–I ...	− 7	37	−·741	87	− ·620						
P–Cl ...	− 4·5	65	......	116	− ·113						
As–Br...	− 5	b. 96	......	120	− ·317	......	......	......	......	206	
As–Cl ...	+39·5	b. 124	......	147	+ ·226	......	......	......	......	229	
Sb–Br...	40	77	−·141	120	− ·144						
Sb–Cl...	84·5	105	......	147	+ ·399						
Si–I ...	−99	−14	......	+ 80	−1·178	111	−·985	......	......	172	
Si–Br ...	−52	+26	.....	113	− ·702	142	−·626	......	......	206	
Sn–I ...	< 9	34	−·950	109	− ·757	123	−·568				
Si–Cl ...	− 7·5	54	......	140	− ·159	167	−·134	......	......	229	
Sn–Br...	+38	74	−·350	142	− ·281	154	−·209				
Pb–I ...	80	116	−·230	128	− ·359						
Sn–Cl...	82·5	102	......	169	+ ·242	179	+·283				
Pb–Br..	127	156	+·370	161	+ ·117						
Pb–Cl...	171·5	184	......	188	+ ·640						
N–I ...	−113	−36	......	+ 17	−1·216	54	......	83	−·802	a. 112	
N–Br ...	− 66	+ 4	......	50	− ·740	85	......	113	−·521	a. 146	
N–Cl ...	−21·5	32	......	77	− ·197	110	......	135	−·109	a. 169	
O–I......	−111	−68	......	− 37	−1·209	−18	......	+10	−·812	58	
O–Br...	− 64	−28	......	− 4	− ·733	+13	......	40	−·531	92	
O–Cl ...	−19·5	0	......	+ 23	− ·190	38	......	62	−·119	115	
Zn–I ...	− 62	2	−·878	46	− ·762	57	− ·649	58			
Zn–Br .	− 15	42	−·278	79	− ·286	88	− ·290	88			
Zn–Cl...	+29·7	76	......	106	+ ·237	113	+ ·202	110			
Hg–I ...	73	50	+ ·805	87	+ ·500	89	+ ·377	76	+·255	a. 112	
Hg–Br .	120	90	+1·405	120	+ ·976	120	+ ·736	106	+·536	a. 146	
Hg–Cl .	164·5	118	......	147	+1·499	144	+1·228	128	+·948	a. 169	

The above 9 Relations can at present be applied in 942 cases, of which 54 (or about 5·7 per cent.) are exceptions. These are distributed as follows :—

	Boiling-points.		Specific gravities.	
	Number of cases in which the rule is applicable.	Number of exceptions.	Number of cases in which the rule is applicable.	Number of exceptions.
Relation 1	73	8	30	1
,, 2	42	0	35	3
,, 3	46	2	31	0
,, 4	42	1	16	1
,, 5	51	0	...	...
,, 6	43	0	25	0
,, 7*a*	35	0	14	0
,, 7*b*	33	3	...	...
,, 8*a*	104	3	45	3
,, 8*b*	......	......	19	2
,, 9	180	20	78	7
Total	649	37 =5·7 per cent.	293	17 =5·8 per cent.

For the reasons stated in my former paper (ibid. p. 10) this is a very small proportion of exceptions ; and even of these no less than 14 are due to the boiling-points of $TeEt_2$ and $SbEt_3$ being too low, and 8 due to the specific gravity of $PbEt_4$ being too low and those of NBu_3 and $SiEt_4$ too high. In the case of the specific gravities, some of the exceptions are undoubtedly owing to these data not being all strictly comparable with one another, since they have neither all been determined at the same temperature, nor at equal distances from the boiling-points.

The above facts show, therefore, that *the physical properties of the alkyl compounds of the elements* (so far as they have been investigated) *obey exactly the same rules as those of the corresponding halogen compounds,* and would consequently allow of general conclusions being drawn and practical applications being made similar to those indicated in my previous paper (ibid. pp. 11, 14, and 19), in connection with the latter compounds, and which it will not be necessary to repeat here.

In my next communication I hope to extend these investigations to the halogen compounds of the hydrocarbon radicals, and subsequently to show how the facts thus obtained may throw light on the nature and *raison d'être* of the Periodic Law.

XXIX. *Origin of Coral Reefs and Islands.*
By JAMES D. DANA, *LL.D.*

[Continued from p. 161.]

PART II.—*The Objections considered.*

THE objections to the Darwinian theory may be considered
in the following order :—

I. Darwin's insufficient knowledge of the facts bearing on
the subject.

II. Subsidence not ordinarily a fact, because methods of
producing barrier reefs and atolls have been brought forward
that do not require its aid.

III. The occurrence of cases of elevation in regions of atolls
and barrier-reefs inconsistent with the subsidence-theory.

IV. No ancient coral-reefs in the geological series have the
great thickness attributed by the subsidence-theory to modern
reefs.

V. Other methods of explanation and their supporting
evidence.

The adverse remarks directed against the idea of a sinking
continent in the Pacific as the initial condition in the coral-reef
subsidence are outside of the present discussion for the reason
stated on the first page of this paper. In the following pages
the objections are first explained, under the above-mentioned
heads, and then follow, in paragraphs lettered *a, b, c,* &c., the
writer's discussions of the several points.

I. *Darwin's Insufficient Knowledge of the Facts.*

In the Address referred to in the opening page of this
article, Dr. Geikie, speaking of Darwin, observes :—" It
should be borne in mind that, compared with more recent
explorers, he did not enjoy large opportunities for investi-
gating coral-reefs." " He appears to have examined one
atoll, the Keeling Reef, and one barrier-reef, that of Tahiti."
" By a gradually widening circle of observations a series of
facts has been established which were either not known, or
only partially known, to Darwin."—The authors appealed to
for the views that are presented as a substitute for Darwin's
are Prof. Karl Semper, who has examined and described reefs
of the Pelew and Philippine Islands ; Dr. J. J. Rein, who
has published on the physical geography of the Bermudas ;
Prof. Alexander Agassiz, who has written on the Florida
reefs and others in that vicinity ; and Mr. John Murray, of
the ' Challenger ' Expedition, whose investigations were made
at Tahiti : all able men in science, whether more learned or

not than Darwin on the special subject under discussion. The facts from "a widening circle of observations" referred to comprise the physical and biological results of deep-sea exploration. The writer is mentioned as one of the "competent observers" who had given "independent testimony" in favour of Darwin's views after "at least equal opportunities of studying the subject," and as he has, in these latter years, looked into the new facts, he has at least a claim to a hearing.

As to Darwin's knowledge, it appears to the writer that the apology offered in the above citations was not needed. In his detailed investigation of Keeling atoll (a good example of atolls, and like all the rest in its principal features) and in his examination of the Tahitian reefs, followed up by a careful study of other atolls and reefs of the ocean through the maps and descriptions of former surveying-expeditions, he had a broad basis for judgment and right conclusions. When the second edition of his work was published in 1874, many of the important facts from deep-sea exploration were already known ; and later he learned of the more recent results ; and he did not recant. A letter of his, of October 2nd, 1879, published by Mr. Semper, while admitting with characteristic fairness the interest of the facts collected by the latter, expresses his continued adherence to the opinion "that the atolls and barrier reefs in the middle of the Pacific and Indian oceans indicate subsidence."

The writer, as his expositor, may be excused for adding here that his own "independent testimony" was based on observations among coral reefs and islands in the Pacific during parts of three years, 1839, 1840, 1841 ; that, besides working among the reefs of Tahiti, the Samoan (or Navigator) Islands, and the Feejees (at this last group staying three months), he was also at the Hawaian Islands ; and in addition, he landed on and gathered facts from fifteen coral-islands, seven of these in the Paumotu Archipelago, one, Tongatabu, in the Friendly Group, two, Taputeuea and Apia, in the Gilbert Group, and five others near the equator east of the Gilbert Group—Swains, Fakaafo, Oatafu (Duke of York's), Hull, and Enderbury Island[*]. The writer may therefore be acquitted of presumption if he states his opinion freely on the various questions that have been brought into the discussion by other investigators. Sympathizing fully with the sentiment expressed in the words, " The example of Darwin's own candour and over-mastering love of truth remains to assure

---

[*] These five islands are on the map of the Central Pacific accompanying Part I. of this paper. Hull's Island is "Sydney" of the writer's Expedition Report.

us that no one would have welcomed fresh discoveries more heartily than he, even should they lead to the setting aside of his work;" and knowing that we are all for the truth and right theory, he has reason to believe that those who have been led to object to Darwin's conclusions will be pleased to have their objections reviewed by one who has a personal know-ledge of many of the facts.

II. *Subsidence not ordinarily a Fact, because Methods of Origin have been brought forward that do not require its aid.*

It is urged that, while subsidence may have happened in several cases, it is not at all necessary to the making of barrier-reefs and atolls ; that "subsidence has been invoked because no other solution of the problem seemed admissible ;" that the "solution" by subsidence "is only an inference resting on no positive proofs" *.

a. Darwin's usual methods were not such as these words imply, and we think that he was true to those methods in his treatment of coral-island facts. Darwin can hardly be said to have "invoked" subsidence. Subsidence forced itself upon his attention. He saw evidence that it was a fact, and the theory came ready-made to him. The proof of subsidence from the relations in form, structure, and history between atolls and the large barrier-islands, like the Gambier Group, Raiatea, Bolabola, and Hogoleu, scarcely admitted, he says, of a doubt; and other facts were all in harmony with it. This, his chief argument, with the enforcing evidence in my Report (see §§ 4 and 10 of Part I. of this paper) is not set aside and not men-tioned in the Address from which the above sentences are cited.

b. Darwin observes that "from the nature of things it is scarcely possible to find direct proof of the subsidence," recognizing the fact that subsidence, unlike elevation, puts *direct* testimony out of sight. But still it has left evidence which he perceived and thought convincing ; and this stands, whatever virtue there may be in other explanations.

Moreover, we have now *direct* testimony for subsidence from the facts brought forward (for another purpose) by Mr. Murray, as is set forth further on.

III. *The Occurrence of cases of Elevation in Regions of Atolls and Barrier-Reefs.*

The fact that elevated reefs and other evidences of eleva-

* Address, page 24.
U 2

tion occur at the Pelews, a region of wide barrier-reefs and atolls, has been presented by Prof. Karl Semper*, after a study of those islands, as an objection to the theory of subsidence; for we have thereby (in the words of the Address) "a cumbrous and entirely hypothetical series of upward and downward movements." Prof. Semper reports the existence of reefs raised 200 to 250 feet above the sea-level in the southern third of the larger of the islands, while the other two thirds exhibit evidence of but little, if any, elevation.

a. Such facts are of the same general character with those of other elevated reefs and atolls discussed in §§ 12, 13, 16 of Part I. and the same explanation covers them. The Pelew region is one of comparatively modern volcanic rocks, and this renders local displacements a probability.

b. The occurrence of great numbers of large and small masses of coral-rock, in some places crowded together, upon the *western* or *leeward* reef of the several Pelew Islands, and of none on the eastern reef, is mentioned as evidence against subsidence and in favour of some elevation; because, Professor Semper says, the strongest wind-waves on the western side are too feeble to break off and leave on the reef such large masses, some of them (as his words imply rather than distinctly state) ten feet thick.

But the difficulty does not exist in fact; for earthquakes may have made the waves. The region just west of the Pelews is one of the grandest areas of active volcanoes on the globe. It embraces the Philippine Islands, Krakatoa and other volcanic islands of the Sooloo sea, Celebes, &c. The agents that could do the work were there in force. To the eastward, in contrast, lie the harmless islands of the Caroline Archipelago, mostly atolls, serving, perhaps, as a breakwater to the Pelews.

The small elevation referred to is therefore not proved by the evidence adduced; and yet it may be a fact without affecting the theory of Darwin, as I have fully illustrated †.

It is important to have in mind that the coral-reef era probably covered the whole of the Quaternary and perhaps the Pliocene Tertiary also; and hence the local elevations that

---

* First in 1868, *Zeitschr. Wissensch. Zool.* xiii. p. 558; additions in *Die Philippinen und ihre Bewohner*, Würzburg, 1869; and still later in his 'Animal Life,' published in Appleton's International Scientific Series in 1881.

† Mr. Semper's objection to the theory of subsidence based on the co-existence of all kinds of reefs in the Pelews—atoll, fringing, and barrier—with no reefs about one island, and from the relative steepness of the submarine slopes on the east and west reefs of an island, have been sufficiently met in Part I.

have taken place in the ocean were not crowded events of a short period.

Moreover, these local elevations in coral-seas are spread over an area of 25,000,000 square miles. As an example of the long distances, the Paumotu Archipelago, consisting of more than eighty atolls and two barrier-islands, and covering about 450,000 square miles, contains only three or four atolls that are over twelve feet high ; and of these, Metia is 250 feet in height, Elizabeth 80 feet, Dean's, probably where highest, 15 or 20 feet. Metia is one of the westernmost, near 148° 13′ W. and 15° 50′ S.; Dean's is 60 miles to the north-north-east of Metia, and Elizabeth is far to the south-east, in 128° W. and 25° 50′ S., or nearly 1450 miles distant from Metia. Locate these points on a continent, and Pacific distances and the length of Pacific chains of atolls will be appreciated.

IV. *No Ancient Coral-reefs have the Thickness attributed by the Subsidence-Theory to Modern Reefs.*

An argument against the subsidence-theory is based by Prof. J. J. Rein* on the alleged fact that the thickness attributed to modern reefs is far beyond that of any such reefs in earlier time ; that is, the thickness is unprecedented. The argument decides nothing. The question is one of geological fact, not to be settled by a precedent. Whether, then, there are precedents or not it is not necessary to consider.

Besides this, it implies a distinction between coral-made and shell-made rocks which does not exist. The coral-reef rock is largely made of shells, and the process of formation for a limestone of shallow-sea origin is essentially the same whether shells or corals are predominant or the sole material. No thick formation of any kind of rock was ever made, or could be made, by shore or shallow-sea operations without a slowly continued subsidence or a corresponding change of water-level.

V. *Other Methods of Explanation, and their Supporting Evidence.*

A. Mr. John Murray, one of the able naturalists of the 'Challenger' expedition, reports the following important results

* Dr. Rein's first memoir on Bermuda appeared in the Senckenberg *Ber. naturforsch. Gesellschaft*, 1869-70, p. 857, and the later in the *Verhandlung des I. deutsch. Geographentages*, 1881, Berlin, 1882. The above argument is from the latter paper, and is given here from the citation by Dr. Geikie, the publication not being accessible to the writer.

from soundings off northern Tahiti, made under his supervision and that of the surveying officers [*].

Along a line outward from the edge of the barrier-reef there were found :—(1) for about 250 yards, a shallow region covered partly with growing corals, which deepened seaward to 40 fathoms ; (2) for 100 yards, between the depths of 40 and 100 fathoms, a steeply but irregularly sloping surface, which commenced with a precipice of 75° and had a mean angle exceeding 45° [†]; then (3) for 150 yards a sloping bottom 30° in angle ; (4) then a continuation of this sloping surface, diminishing in a mile to 6°, at which distance out the depth found was 590 fathoms (3540 feet).   Over the area (2), or the 100 yards between 40 and 100 fathoms, the bottom was proved to be made of large coral-masses, some of them "20 to 30 feet in length," along with finer débris ; outside of this, of sand to where the slope was reduced to 6° ; and then of mud, composed " of volcanic and coral-sand, pteropods, pelagic and other foraminifers, coccoliths, &c."

These observations have great significance.   They show (1) that the feeble currents off this part of Tahiti carry little of the coral débris in that direction beyond a mile outside of the growing reef ; (2) that a region of large masses of coral-rock and finer material occurs at depths between 240 and 600 feet ; (3) that, a mile out, the bottom has the slope nearly of the adjoining land, and in this part is covered with the remains of pelagic life.

From the second of these facts—the great accumulation of coral-blocks below a level of 240 feet—Mr. Murray draws the conclusion that, in the making of fringing, barrier, and atoll reefs, the widening goes forward (*a*) by making first upon the submarine slopes outside of the growing reef a pile of coral-débris up to the lower limit of living reef-corals ; and then (*b*) by building outward upon this accumulation as a base.

He also announces, after speaking of other causes influencing the growth of corals, the more general conclusion that " it is not necessary to call in subsidence to explain any of the characteristic features of barrier-reefs and atolls;" and concludes that his views " do away with the great and general subsidences " appealed to by Darwin.

a. The widening-process, in the first conclusion, had previously been a part of the Darwinian theory ; for, as

[*] Proc. Edinburgh Roy. Soc., Session 1879-80, p. 505.
[†] Dr. Geikie gives in his paper a section of the soundings, " on a true scale, vertical and horizontal," and in it the upper steepest part of this 100 yards has a slope of about 75°.

stated in § 10 (Part I.), a fringing reef, where no subsidence is going on, widens above and steepens its seaward-slope, and it could do this only by the process described : that is, by building out upon a base of débris, or, more correctly, upon true coral-reef rock made by the gradual consolidation of the débris [*].

b. The broader conclusion Mr. Murray does not sustain by a mention of special facts from the soundings, tending directly to meet the question of change of level, but by attempting to show that through the eroding action of currents and other means (as had been argued by Prof. Semper), in connection with the process already explained, reefs of all kinds can be made from submarine banks without aid from subsidence.

In this place I confine myself to the question as to the fact of subsidence. The only direct argument presented against subsidence is contained in the statement, that the very broad shore-plain of Tahiti shows that " the island has not in recent times undergone subsidence," and may indicate a slight elevation ; and in this he sustains the earlier statement of my report, which says (p. 293) that the broad shore-plain of Tahiti probably overlies in some parts the fringing reef ; and (p. 300) the shore-plain, if built upon reefs, as I was assured, may afford proof of a rise of one or two feet." But this admission, as I have explained for other cases of local elevation, is in no way opposed to the theory of subsidence.

c. The kind of submarine slopes to be looked for off reefs is illustrated by the soundings, as Dr. Geikie indicates. But it is interesting to note that the facts, while very important, sustain instead of correcting those announced by earlier observers. Beechey and Darwin make the mean slope about 45°, and my report says 40° to 50°. I have assumed for the slope of the bottom outside of the reef-limit the same angle as for the surface-slope of the island just above the water-level : 5° to 8° off Tahiti, of which 5° is accepted as most correct, and 3° to 5° off Upolu[†] ; and the assumption as regards Tahiti is sustained by the ' Challenger ' soundings. My Report states (from the Expedition surveys) that off Upolu the bottom " loses more and more in the proportion of coral-sand till we finally reach a bottom of earth," and introduces this as an argument against the indefinite drifting of coral-sands into the deep ocean [‡] ; and this argument the Tahiti soundings sustain.

With reference to the occurrence off some shores of precipi-

---

[*] My Expedition Geological Report, pp. 131, 132, where figures are given illustrating the effect of widening.
　[†] Page 47.　　　　　　　　　　　　　　[‡] Page 154.

tous submarine slopes, the ' Challenger ' soundings give definite facts as to one case.   They leave undisturbed the previously reported cases of like steepness at greater depths : for example, the sounding of Captain Fitzroy at Keeling atoll (while Darwin was there), 2200 yards from the breakers, in which no bottom was found at a depth of 1200 fathoms, but the line was partly cut at a depth between 500 and 600 fathoms ; the sounding by the Wilkes Expedition off Clermont Tonnere (Paumotu Archipelago), where the lead, brought up an instant at 350 fathoms and then dropped off again, descended to 600 fathoms without reaching bottom, and came up bruised, with small pieces of white and red coral attached ; a sounding by the same Expedition, a " cable's length " from Ahii, in which the lead struck a ledge of rock at 150 fathoms and brought up finally at 300 fathoms *.   All the older soundings need to be repeated ; but there must be enough truth in those quoted to warrant the remark that the force of Darwin's argument for subsidence from the steepness of the submarine slopes about atolls is not weakened by the ' Challenger ' results.

d. But the chief interest of the ' Challenger ' soundings consists in their affording " direct " proof, " positive " proof, of *much subsidence* ; a kind of proof that subsidence sinks out of sight, and which soundings may yet make available in many similar cases.

That belt of coarse débris—including " masses 20 to 30 feet " long—was found over the steeply sloping bottom at depths between 240 and 600 feet.   These depths are far below the limit of forcible wave-action.   They are depths where the waters, however disturbed above by storms, have no rending and lifting power, even when the bottom is gradually shelving ; depths, in this special case, against a slope which for 100 yards is 75° in its upper part, and in no part under 45°, the vertical fall being 360 feet in the 100 yards. Strokes against the reef-rock thus submerged, and under such conditions, would be extremely feeble.   Waves advancing up a coast, whether storm-driven waves or earthquake waves, do little rock-rending below the depth to which they can bare the bottom for a broadside plunge against the obstacle before them, although the velocity gives them transporting power to a greater depth.   It is the throw of an immense mass of water against the front, with the velocity increased by the tidal flow over a shelving bottom,—the rate sometimes amounting, according to Stevenson, to 36 miles an hour or 52·8 feet a second,—together with the buoyant action of the water, that produces the great effects.

* *Ibid.* p. 55.

A vertical surface below the sea-level of 20 feet made bare for the broadside stroke is probably very rarely exceeded even in the case of earthquake-waves ; and with storm-waves, or recorded earthquake-waves, the displacement of the water at a depth of 240 feet would be at the most only a few inches. I saw on atoll reefs no upthrown masses of coral-rock over ten feet in thickness and twenty feet in length or breadth. It is therefore plainly impossible that such a belt of débris should have been made at its present level, or even at a depth of 20 feet ; and hence the débris affords *positive proof of a large subsidence during some part of the reef-making era.*

The existence of the belt of débris may be explained as follows :—If the reef now at a depth of 240 feet were at the sea-level as the sea-level reef, and subsidence were not in progress for a period, the very steep front of the reef now just below the 240-foot level might have resulted from the widening that would have gone forward. And under such conditions, the action of the occasional extraordinary waves might have torn off masses from the front which would have tumbled down the steeply sloping surface until the belt of débris had been formed. Then, with a renewal of the slow subsidence, the thickening of the reef would have been resumed and gone on to its final limit, and the rendings of the great waves found lodgment at higher levels. The masses now on atoll reefs must be from comparatively recent up-throws.

This *direct* evidence of subsidence from Tahiti renders it reasonable to make subsidence in atoll-making a general truth. It is nevertheless desirable that facts of the kind should be multiplied. The abrupt descent in the submarine slopes of reefs detected by Fitzroy at a depth below 3000 feet, and those reported by the Wilkes Expedition at depths of 2100 and 900 feet, seem to indicate a similar rest at the sea-level, and consequent reef-widening in the course of a progressing subsidence ; and proof of this may yet be found in belts of coarse coral-rock débris at the foot of the precipices. Such a period of rest would lead to the forming of submarine precipices in different regions contemporaneously at different depths according to the rate of subsidence of the part of the subsiding area.

B. From facts observed about the Florida reefs, Lieutenant E. B. Hunt, U.S.N., announced, in 1863 *, the conclusion that these reefs had received their westward elongation

* Silliman's American Journal [2] xxxv. p. 197.

through the westward " sweep " of an eddy current to the Gulf Stream. The subject, nearly twenty years afterwards, was more thoroughly investigated by Mr. Alexander Agassiz, and the same conclusion reached *. Mr. Agassiz made also another important observation—that this current is an abundant carrier of marine life for the feeding of the coral animals, and so accelerates the coral-growth and accumulation in its direction. Combining with these effects others hereafter considered, Mr. Agassiz expresses, like Mr. Murray and Mr. Semper, the further conclusion, that all kinds of reefs—atoll, fringing, and barrier—may be made without aid from subsidence.

a. The facts presented by Lieutenant Hunt, and more fully by Mr. Agassiz, with regard to the effects of the eddy current of the Gulf-Stream, show that coral-reefs may be elongated, and also that inner channels may be made, by the drifting of coral-sands. But the action with coral-sands is essentially the same as with other sands ; and illustrations of this drifting process occur along the whole eastern coast of North America from Florida to Long Island. We there learn that drift-made beaches run in long lines between broad channels or sounds and the ocean ; that they have nearly the uniform direction of the drift of the waters, with some irregularities introduced by the forms of the coast and the outflow of the inner waters, which are tidal and fluvial and have much strength during ebb tide. The easy consolidation of coral-sands puts in a peculiar feature, but not one that affects the direction of drift accumulation.

b. The great barrier-reef off eastern Australia, a thousand miles long, has some correspondence in position to the sand-reefs off eastern North America. But it is full of irregularities of direction and of interruptions, and follows in no part an even line. In the southern half, it extends out 150 miles from the coast and includes a large atoll-formed reef ; in the northern half, the barrier, while varying much in course, is hardly over 30 miles from the land. There is very little in its

---

* On the Tortugas and Florida Reefs, by A. Agassiz, Trans. Amer. Acad. xi. 1883.

Professor Louis Agassiz's account of the Florida reefs was published in the U. S. Coast Survey Reports of 1851 and 1866, and reproduced in vol. vii. of the Memoirs of the Museum of Comparative Zoology. It gives an excellent description of the Florida reefs, and of the action of boring animals and other injurious agents on corals, and reaches the conclusion that the reef has been raised to its present level and thickness by wave and current action, without the aid of elevation or subsidence. The argument is based on such observations as could be made over the surface of the reefs and the adjoining sea-bottom, and bears on the question of the necessity of subsidence, and not on the fact of subsidence.

form to suggest similarity of origin to the drift-made barriers of sand.

c. In the Pacific Ocean, the trends of many of the coral-island groups and of the single islands do not correspond with the direction of the oceanic currents, or with any eddy currents except such as are local and are determined by themselves.

Near longitude 180°, as the map of the Central Pacific (see Part I.) illustrates, the equator is crossed by the long Gilbert (or Kingsmill) group, at an angle with the meridian of 25° to 30°, and not in the direction of the Pacific current, which is approximately equatorial. This obliquely crossing chain of atolls is continued northward in the Ratack and Ralick Groups (or the Marshall Islands), making in all a chain over 1200 miles long ; and, adding the concordant Ellice Islands on the south, and extending the Ratack line to Gaspar Rico, its northern outlier, the chain is nearly 2000 miles long. Nothing in the direction of the long range, excepting local shapings of some of the points about the atolls, can be attributed to the Pacific currents. Moreover, the diversified forms of the atolls have no sufficient explanation in the drift process.

d. Further, drifting by currents may make beaches and inner channels whether subsidence is going on in the region or not, and are not evidence for¦ or against¦ either a movement downward or upward. Sandy Hook, the long sandy point off the southern cape of New York harbour, has been undergoing (as the U. S. Coast Survey has shown) an increase in length, or rather variations in length, through the drifting of sands by an outside and an inside current ; and this is no evidence that Professor G. H. Cook is wrong in his conclusion that the New Jersey coast is slowly subsiding.

e. But even *in this region of Florida we have strong evidence of a great subsidence during the coral-reef era*, and all the subsidence that the Darwinian theory demands.

In a very valuable paper by Mr. Agassiz, published in 1879 in the Bulletin of the Museum of Comparative Zoology *, the author points out that the South American continent, in comparatively recent geological times, had connection with the West-India Islands through two lines : (1) one along a belt from the Mosquito Coast to Jamaica, Porto Rico, and Cuba ; and (2) the other through Trinidad to Anguilla, of the Windward Islands. He sustains the conclusion by a review of the soundings made by the steamer ' Blake,' under the command of

---

* An abstract of the paper is contained in Silliman's American Journal [3] xviii. p. 230 (1880).

J. R. Bartlett, U.S.N., and a consideration of the facts connected with the distribution of marine and terrestrial species. As the soundings show, the former of the two connections requires for completeness an elevation of the region amounting to 4060 feet over the part south of Jamaica, 4830 feet between Jamaica and Hayti, and 5240 feet between Hayti and Cuba. The other line of connection requires an elevation of 3450 feet. An open channel, as he observes, would thus be left between Anguilla and the Virgin Islands, where there is now a depth of 6400 feet. The close relations in the existing fauna of the Gulf to that of the Pacific waters prove that it continued to be a salt-water gulf through the era of elevation.

Mr. Agassiz infers that the connection of the West-India Islands with South America existed before the Quaternary era. But there are other facts which seem to prove that it was continued into, or at least was a fact in, the Quaternary.

The opinion as to a connection of the Windward Islands with South America in the Quaternary was presented by Prof. E. D. Cope in 1868, and earlier, as he states, by Pomel, on the ground of the discovery in the caves of Anguilla of a species of gigantic Rodent related to the Chinchilla, as large as the Virginia Deer, and nearly equalling the Quaternary *Castoroides* of Ohio [*]. Further, De Castro, as cited by Dr. J. Leidy in his 'Mammalian Fauna of Dakota and Nebraska,' 1869, announced, in 1865, a gigantic Sloth of the "Quaternary," from Cuba, which he referred to the genus *Megalonyx*, and Dr. Leidy named *Megalocnus rodens*, proving a Quaternary connection between the continent and Cuba.

The fact of an elevated condition of the region sufficient to make Cuba and Anguilla part of the continent during the earlier Quaternary, if not in the Pliocene also, is thus made quite certain. This is fully recognized by Wallace [†]. Such a condition could hardly have existed without a large elevation also of Florida, though probably not, as Mr. Agassiz holds, to the full amount of the depression between it and Cuba (nearly 3000 feet), because Cuba is most closely related in fauna to South America. The subsidence which brought the region to

[*] Proc. Philad. Acad. Nat. Sci. 1868, p. 313, and Proc. Philad. Amer. Phil. Soc. 1869, p. 183; also 'Smithsonian Contributions to Knowledge,' 30 pp., 4to, with 5 plates, Washington, 1883. The last paper (prepared in 1878) contains descriptions of the following species from the Anguilla bone-cave :—*Amblyrhiza inundata*, Cope (the large Rodent announced in 1869), *A. quadrans*, Cope, *A. latidens*, Cope, an Artiodactyl apparently of the *Bovidæ* and a little smaller than *Ovis aries*. With them was obtained an implement (" a spoon-shaped scraper or chisel ") made of the lip of the large *Strombus gigas*.

[†] Geograph. Distrib. of Animals, ii. pp. 60, 78.

the present level was consequently within the coral-reef period. It is hence hardly to be doubted that the making of the Florida, Bahama, and other West India coral-reefs was going on during the progress of a great subsidence. None of the facts mentioned by observers are opposed to this view.

It is of interest to note here that on Cuba and Jamaica there are *elevated* coral-reefs, the highest on Cuba 1000 feet above the sea, according to Mr. Agassiz, and probably at one point 2000, according to Mr. W. O. Crosby's observations *, and on Jamaica 2000 feet, according to Mr. Sawkins ; indicating that there have been upward movements subsequent to the downward. Mr. Crosby argues that the great thickness of the now elevated reefs could have been produced only " during a progressing subsidence ;" so that " we have apparently no recourse but to accept Darwin's theory."

C. It has been urged by Mr. Semper, Dr. J. J. Rein, Mr. A. Agassiz, Mr. Murray, Dr. Geikie, and others, that since the growing calcareous deposits of the sea-bottom are slowly rising toward the surface by successive accumulations of the shells and other débris of marine species, they may have been built up locally in various regions of the deep seas (as they actually are now about some islands) until they were near enough to the surface to become next a plantation of corals ; and that in this way atolls became common within the area of the tropical oceans. The method is regarded as setting aside subsidence.

a. The advocates of this hypothesis have not pointed to such a mound now approaching the ocean's surface on the western border of the Gulf-Stream, where the depth over the remarkably luxuriant region is least ; and none over any part of the tropical Pacific. It is suggested that the Chagos Bank may be one example ; but it is not known to be so. Professor Semper states that he found evidence of pelagic life, instead of modern corals, in the lower part of the elevated reefs of the Pelews. Dr. Geikie cites from letters by Dr. Guppy in ' Nature ' of Nov. 29, Dec. 6, 1883, and Jan. 12, 1884, the fact that in elevated reefs on the Salomon Islands, 100 and 1200 feet high, the coral-rock forms a comparatively thin layer over impure earthy limestone abounding in foraminifers and other pelagic organisms such as Pteropods. Such obser-

* Proc. Boston Soc. Nat. Hist. xxii. p. 124, (1882), and in abstract in Silliman's American Journal, xxvi. p. 148 (1883).

vations have great interest, but they only prove that, in coral-reef seas, corals will grow over any basis of rock that may offer where the water is right in depth, and do not nullify any of the evidences of subsidence. This point should be kept before the mind in all future study of coral-reef regions. Borings in coral-islands, as recommended on a former page, are the true means of investigating it.

b. The old hypothesis that atolls may have been built upon the summits of submerged mountain-peaks, or volcanic cones at the right distance under water for growing reef-corals, or, if not at the right level, brought up to it by other organic depositions, or down to it by abrasion, is urged by Mr. Murray.

This writer observes that " the soundings of the ' Tuscarora ' and ' Challenger' have made known numerous submarine elevations ; mountains rising from the general level of the ocean's bed at a depth of 2500 or 3000 fathoms, up to within *a few hundred fathoms* of the surface." But " a few hundred fathoms," if we make few equal 2, means 1200 feet or more, which leaves a long interval yet unfilled *.

It is also urged that some of the " emerged volcanic mountains situated in the ocean-basins " may have been wholly swept away and left with a few fathoms of water above them. But this is claiming more from the agents of erosion than they could possibly have accomplished, as the existence of an atoll in the ocean and the examples on coasts of wave and tidal action prove.

D. To give completeness to the hypothesis which makes barrier and atoll islands out of submarine banks (whether these banks have a basis of volcanic or other rocks, or of calcareous accumulations), it is necessary to show that the waters of the waves and currents can make barrier islands and atolls out of such banks without subsidence ; and explanations to this effect have been given.

It is urged, in agreement with Darwin, that the outer por-

---

* The actual depths over the elevations in the 'Tuscarora' section between the Hawaian Islands and Japan, numbering them from east to west, are as follows :—1, 11,500 feet ; 2, 7500 feet ; 3, 8400 feet ; 4, 12,000 feet ; 5, 9000 feet (this seven miles west of Marcus Island) ; 6, 9600 feet. Whether ridges or peaks the facts do not decide ; probably the former. No. 1 has a base of 185 miles, with the mean eastward slope 40 feet per mile ($=1:132$), and the westward 128 feet per mile. No. 2 has a breadth of 396 miles, with the mean eastern slope mostly 37 feet per mile, but 51 feet toward the top, and the westward, 55 feet per mile ($=1:96$). No. 3 was the narrowest and steepest, it being about 100 miles broad at base, and having the mean eastern slope 192 feet per mile and the mean western 200 feet.

tions of reefs increase faster than the inner, owing to the purer water about them and the more abundant life for food ; that the inner parts are not only at a disadvantage in these respects, but suffer also from coral débris thrown over them. They add to these causes of unequal growth mentioned by Darwin, the solvent and abrading action of the waters.

It is hence concluded that, under these conditions, the simple bank of growing corals may have a depression made at the centre, which, as the process continues, will become a lagoon basin, and the reef thereby an atoll with a shallow lagoon ; that the atoll, so begun, may continue to enlarge through the external widening of the reef and the further action of current-abrasion and solution within : or, in the case of fringing reefs, that the change may go on until the reef has become a barrier-reef, with an inner channel and inner reefs. It is admitted that subsidence may possibly have helped in the case of the deepest lagoons.

Dr. Geikie expresses his opinion on the subject thus :—" As the atoll increases in size the lagoon becomes proportionally larger, partly from its waters being less supplied with pelagic food, and therefore less favourable to the growth of the more massive kinds of corals, partly from the injurious effects of calcareous sediment upon coral-growth there, and partly also from the solvent action of the carbonic acid of the sea-water upon the dead coral."

Mr. Semper gives examples of the effects of currents at the Pelew Islands, stating that, by striking against or flowing by the living corals, they make the reef grow with steeper sides and determine its direction, and urging that abrasion and solution have made, not only the deep lagoon-like channels, but the deeper channels between the islands. He holds that in Kriangle, which he describes as a true atoll with no channel leading into the lagoon from the sea, the lagoon may have been " the result of the action of currents on the porous soil during a period of slow upheaval*. He says, further, that the large channel in the main island of the group " forty fathoms deep and many miles wide," " finds an easy explanation on the assumption of an upheaval ;" it became " wider in proportion as the enclosed island, consisting of soft stone [tufa], was gradually eaten away ; and during slow upheaval it would continue to grow deeper in proportion as the old porous portions of the reef and the rock in which it was forming were more and more worn down by the combined action of boring animals and plants, and of the currents

* 'Animal Life,' pp. 269, 270.

produced by the tides and by rain." Mr. Semper refers to the dead depressed tops of some masses of Porites near tide-level, as the effects of the deposit of sediment over the top of the living coral, and of erosion by the waves and exposure to rains while the sides continued to grow ; and the fact is made an example on a very small scale of atoll-making. Other examples of the action of currents, sediments, boring species, and the solvent action of carbonic acid in the waters are mentioned by Mr. Agassiz, in his excellent account of the " Tortugas and Florida reefs."

a. The theory, if satisfactory, accounts not only for the origin of an atoll, but for the origin of atolls of all sizes, shapes, and conditions, and for great numbers of them in archipelagos and chains ; not only for channels through fringing reefs, like those that abrasion in other cases makes, but for all the irregular outlines of barriers, for the great barriers reaching far away from any land, and for the positions and indented coasts of the small included lands. Is it a sufficient explanation of the facts ?

b. The currents that influence the structure of reefs are : (1) the general movement or drift of the ocean, in some parts varying with seasonal variations in the winds ; (2) the currents connected with wave-action and the inflowing tide over a shelving bottom ; (3) the currents during the ebb, flowing out of channels ; together with (4) counter-currents. Each region must have its special study in order to mark out all the local effects that currents occasion. Such effects are produced whether a secular subsidence is in progress or not, and hence a particular review of the subject in this place is unnecessary.

The shaping of the outside of the reef and the determination of the width and level surface of the shore platform are due chiefly to the tidal flow and the accompanying action of wind-waves, as explained in § 17 of Part I.*

---

* Since the first part of my paper was published I have observed in an article by Mr. A. R. Hunt, in the Scientific Proceedings of the Royal Dublin Society, iv. p. 254, January 1885, the remark, referring to a statement of the above fact in my' Manual of Geology,' that the " statement, though strictly in accordance with Mr. Russel's theory, has, so far as I can ascertain, no foundation in fact." The statement, as I have said (and as I illustrate in my ' Geology '), was but the statement of a fact observed by me first in 1839 on the coasts of Australia and New Zealand, without a thought of any theory ; and part of the explanation is overlooked by Mr. Hunt. I *observed* that the first waters of the incoming tide swelled over the sandstone platform (which was a hundred yards or more wide off the Port-Jackson Heads), and became thus a protector of the sandstone *platform* from breaker strokes ; and that the lower part of the sandstone *bluff* to a height a little above high tide was hollowed out by the strokes

The current that accompanies the ebb is locally the strongest. Owing to the great width of many barrier-reefs and of the channels and harbours within them, the tide flows in over a wide region. At the turn in the tide the waters escape at first freely over the same wide region ; but, with a tide of but two or three feet, there is but little fall before the reef— which lies at low-tide level and a little above it—retards it by friction ; and thus escape by the open entrances is increased in amount and in rate of flow.· The facts are the same in atolls where the lagoons have entrances*.

---

of the breakers. A similar erosion near high-tide level of the great coral masses standing on the coral-rock platform of atolls I also observed while among the Paumotu Islands. Prof. A. E. Verrill informs me that he has seen examples of the same action on a grand scale about the island of Anticosti in the Gulf of St. Lawrence. The observations do not appear to me to be at variance with the principles laid down in Mr. Hunt's valuable paper ; they require only his recognition of a tidal effect which he does not fully consider, and which British seas cannot illustrate.

To produce a platform, (1) the rock-material exposed to the flow of the tide and the breakers must be firm enough to resist wear during the early part of the flow, and, at the same time, soft enough to allow the striking breakers to cut into the base of the bluff, or shear off the projecting ledge ; and (2) the region must not be one of very high tides or stormy seas, for, in such regions of forceful waves and tides, the movements are too often of the destructive kind through the whole continuance of the flow leaving no chance for the protection a platform needs. Loose sand-deposits are too soft ; they are worn off below the sea-level and changed in surface by storms ; but some firmer kinds may make a low-tide flat in a bay where the tides are small. Coral-reef rock, the material of the atoll platform, has the hardness and solubility in carbonated sea-water of ordinary limestone. The rock of the Port-Jackson Heads is a friable sandstone. At the Bay of Islands, New Zealand, the platforms occur in an argillaceous rock, which becomes soft and earthy above by weathering, but is unaltered and firm below because kept wet (*loc. cit.* p. 442). At the Paumotus the tides are two to three feet high, and the platform usually 100 yards or more wide ; at the Phœnix Group the tides are five to six feet high and the platform mostly 50 to 70 yards wide ; at the Port-Jackson Heads, the ordinary tides are six feet high and the platform 50 to 150 yards wide ; at the Bay of Islands (in the sheltered waters of the bay), the tides are eight feet high and the platform is under 30 yards wide.

* The currents of the tropical Pacific Ocean are of very unequal rate in its different parts, and very feeble in the Paumotu Archipelago and the Tahitian and Samoan regions. Capt. Wilkes reports that in the cruise of the Expedition through the Paumotu Archipelago to Tahiti, a distance of a thousand miles, during a month from August 13 to September 13, 1839, the drift of the vessels was only 17 miles ; and that during fourteen days in the first half of October, between Tahiti and Upolu of the Samoan group, nearly 1800 miles, the drift was only 43 miles. The 'Challenger,' on her route from the Hawaian Islands to Tahiti, found, between the parallel of 10° S. and Tahiti, " the general tendency of the current westerly, but its velocity variable ;" between the parallels of 10° S.

c. Examples of massive corals having the top flat or depressed and lifeless, while the sides are living, are common in coral-reef regions, wherever such corals are exposed to the deposition of sediment, and where they have grown up to the surface so that the top is bare above low tide. A disk of Porites, having the top flat and the sides raised (owing to growth), so as to give it an elevated border, is figured on plate lv. of my Report on Zoophytes. Many such were found in the impure waters of a shore-reef at the Feejees. At Tongatabu one flat-topped mass of Porites was twenty-five feet in diameter; and both there and in the Feejees, others of Astræids and Meandrinas measured twelve to fifteen feet in diameter.

Over the dead surfaces, as Mr. Semper observes, the coral may be eroded by the solvent action of the waters, and especially where depressions occur to receive any deposits, and boring animals may riddle the coral with holes or tubes. But generally the erosion is superficial; the large masses referred to showed little of it. Such dead surfaces in corals are generally protected by a covering of nullipores and other incrusting forms of life, and the crusts usually spread over the surfaces *pari passu* with the dying of the polyps.

d. Every stream, says Mr. Semper (when explaining, as cited on a preceding page, the origin of the deep channel of the large Pelew island, whose depth is " 35 to 45 fathoms "), " has a natural tendency to deepen its bed." But there is a limit to this action. The eroding or deepening power of a stream

---

and 6° N., the direction was westerly with "the average velocity 35 miles per day, the range 17 to 70 miles per day," the maximum occurring along the parallel of 2° N. Further west, about the Phœnix group, the equatorial current as described by Mr. Hague (*loc. cit.* p. 237), has " a general direction of west-south-west and a velocity sometimes exceeding two miles per hour." At times it changes suddenly and flows as rapidly to the eastward. The drifting of the sands about Baker's Island (in latitude 0° 13′ N., longitude 176° 22′ E.) has much interest in connection with this subject of current-action, and the facts are here cited from Mr. Hague's paper. The west side of the little island ($1 \times \frac{2}{3}$ m. in area) trends north-east, and the southern east-by-north, and at the junction a spit of sand extends out. During the summer the ocean swell, like the wind, comes from the south-east, and strikes the south side; and consequently the beach sands of that side are drifted around the point and heaped up on the western or leeward side, forming a plateau along the beach two or three hundred feet wide, and eight or ten feet deep over the shore-platform. With October and November comes the winter swell from the north-east, which sweeps along the western shore; and in two or three months the sands of the plateau are all drifted back to the south side, which is then the protected side, extending the beach of that side two or three hundred feet. This lasts until February or March, when the operation is repeated.

through abrasion and transportation is null or nearly so below the level of its outlet. A basin or channel 45 fathoms (270 feet) deep, with an outlet of much less depth, could not be deepened by such means or protect itself from shallowing. The depth of the outlets is not stated, except that they are said to be ship-channels. Moreover, with a tufa bottom, solution could not contribute to the removal, since carbonated waters, although decomposing the tufa, dissolve very little of its ingredients. An elevation in progress would result in making of the channel a closed lake, and finally dry land.

For the same reason, the small atoll, Kriangle, having, as described, a *closed* lagoon, could have no deepening of the lagoon from abrasion by tidal currents or wave-action during the progress of an elevation. And if a lagoon have an outlet, the rapid current of the ebb would be confined to the narrow passage-way and a portion of the bottom near it ; through the larger part of the lagoon, as in any other lake, the waters would have scarcely perceptible motion, and therefore slight energy for any kind of work. Hence a lagoon would lose very little by this means, and shallowing would go on unless there were great loss through the *solvent action* of the waters. An elevation would only hurry the shallowing and end in emptying the lagoon.

e. Erosion through solvent action is promoted by the presence in the waters both of carbonic acid and organic acids. The material within reach of the tides or waves exposed to this action is dead corals and shells, or their débris, and bare coral rocks, occurring over—(1) the outer region of living corals and for a mile or so outside ; (2) the shore platform and the reef, bare at low tide, on which there is comparatively little living coral ; and (3) the lagoon basin. There is nothing in the material within the lagoon to favour solution more than in either of the other two regions ; in fact, the platform and bare reef are most exposed to the action because of the small amount of living corals over them. The outside waters take up what they can through the carbonic acid they contain, and supply thereby the wants of the lime-secreting polyps, shells, &c., and carry on the process of solidification in the débris ; the same waters move on over the atoll reef and take up more lime as far as the acid ingredient is present ; and then they pass to the lagoon for work similar to that outside, with probably a diminished amount of free carbonic acid, on account of the loss over the reef-ground previously traversed.

The lagoon basin is not, therefore, the part of the atoll that loses most by solution, any more than by abrasion and trans-

portation. The outer reefs suffer the most ; and yet, if the
island is not subsiding at too rapid a rate, they keep extending
and encroaching on the ocean, instead of wasting through
the drifting into the ocean at large of calcium carbonate in
grains and solution ; and the shore-platform also preserves
its unvaried level notwithstanding the daily sweep of the
tidal floods, and the holes that riddle its outer portions.

The remarks, " It is a common observation in atolls
that the islets on the reefs are situated close to the lagoon
shore ;" and such " facts point out the removal of matter which
is going on in the lagoons and lagoon channels," * I know
nothing to sustain. The width of the shore-platform on the
seaward side is always greater than that on the lagoon side ;
but the outside shore-platform has its width determined by
tidal and wave action, and this action is powerful on the
ocean side, and feeble on the lagoon side ; it produces a high
coarse beach on the outside as the inner limit of the platform,
and a finer, lower, and much more gently sloping beach on
the inside. The amount of erosion is far greater, as it should
be, on the side of the powerful agencies.

f. The loss to the lagoon by abrasion and solution *is reduced
to a minimum, in the majority of atolls, by the absence of lagoon
entrances*, which leaves them with only concealed leakage
passages for slow discharge.

Nine tenths of atolls under six miles in length (or in longer
diameter), half of those between six and twenty miles, and
the majority of all atolls in the Pacific Ocean, have no en-
trances to the lagoon a fathom deep ; and the larger part of
those included in each of these groups have no open entrances
at all.

For evidence on this subject, I refer to the Wilkes Expedi-
tion Hydrographic Atlas. This Atlas contains maps of nearly
sixty coral-islands from the surveys of its officers, drawn on
a large scale (one or two miles, rarely four, to the inch).

Out of the number, nine, ranging from 1½ to 3 English
miles in the longer diameter of the reef, *have no lagoon*, but
only a small depression in its place ; two of these take in
water at high tide, and the rest are dry.

Of those *under six miles in length having lagoons*, seventeen
in number, sixteen are represented as having *no entrances to
the lagoon* at low tide ; and the one having an entrance is
5 × 4 miles in size. The smallest is about a mile in diameter.

Of those that are *six miles or over* in length, twenty-nine
in number, seventeen have channels and twelve have none.

* Mr. Murray, *loc. cit.* p. 515.

Those having channels are mostly over ten miles in length. A list of them is here given with their sizes, and also the proportion of the reef around the lagoon which is under water above third tide, and bare at low tide, a feature of much interest in this connection.

ELLICE GROUP.—Depeyster's : 6 × 6 m.; three fourths of the encircling reef bare. Ellice's : 9 × 5 m. ; three fourths bare.

GILBERT GROUP.—Apia: 17 × 7 m.; half bare. Tarawa : 21 × 9 m. ; half bare. Taritari : 18 × 11 m. two thirds bare Apamama : 12 × 5 m.; half bare. Taputeuea ; west side mostly submerged.

MARSHALL ISLANDS (northern).— Pescadores : 10 × 8 m. ; four fifths bare. Korsakoff : 26 m. ; four-fifths bare.

PAUMOTUS.—Peacock ; 15 × 7 m. ; nearly all wooded. Manhii : 13 × 5 m. ; nearly all wooded. Raraka : 6 × 9 m. ; three fourths wooded. Vincennes : 13 × 9 m. ; mostly wooded. Aratica : 18 × 11 m. ; three fifths bare. Tiokea : 18 × 4 m. ; two thirds wooded. Kruesenstern's : 16 × 10 m. ; mostly wooded. Dean's (or Nairsa): 53 × 18 m. ; half or more bare.

g. The absence of open channels in so large a proportion of lagoons, and especially in lagoons of the smaller atolls, appears to be fatal to the abrasion-solution theory. The method of enlarging atolls through currents and solution can act only feebly, if at all, where waters have no free outlet ; and this is eminently so with the smaller atolls which have been assumed by the theory to be most favourable in purity of water and in abundant life for progress ; if the small cannot grow, the large lagoons cannot be made from them by the proposed method.

Reverse the method, letting the large precede the small (as under the subsidence theory), and then we have a consistent order of events. We have large atoll reefs with several large entrances (like the great barrier-reef about a high island in this and other respects) gradually contracting, and the entrances concurrently narrowing through the growing corals and the consolidating débris, in spite of the efforts of abrasion and solution to keep them open and make them deeper ; and, afterwards, the atoll becoming still smaller until the entrances close up; and, finally, the lagoon-basin is reduced to a dry depression with nothing of the old sea-water remaining except, perhaps, some of its gypsum.

h. Instead of small lagoons having the purest waters, the reverse is most decidedly and manifestly the fact, and this

accords with the reversal in the history just suggested. Since atolls of middle and larger size commonly have one third to two thirds of the encircling reef covered with the sea at one-third tide, making the ocean and lagoon for more than half the time continuous, the large lagoon in such a case has as pure water as the ocean, and commonly as good a supply of food-life, and sometimes as brilliant a display of living corals. But in the smaller atolls, the area of the lagoon has little extent compared with the length and area of the encir-cling reef; coral-sands and other calcareous material con-sequently have possession of the larger part of the bottom, and the waters, since they are less pure than those outside, contain fewer and hardier kinds of corals and less life of other kinds. They are exposed, also, to wider variations of temperature than the outer, with injury to many species; and at lowest tides may become destructively overheated by the midday sun, as many a plantation of corals with dead tops for a foot or more bears evidence. In the smallest atolls, the lagoons are liable also to alternations of excessive saltness from evapo-ration and excessive freshness from rains, and consequently no corals can grow inside, though still flourishing well in the shallow sea about the outer reef. The above are the facts, not the suggestions of theory.

i. We read :—" So great is the destructive and transporting influence of the sea under the combined or antagonistic work-ing of tides, currents, and wind-waves that the whole mass of the reef, as well as the flats and shoals inside, may be said to be in more or less active movement"*. This description of the Tortugas reefs is not applicable to the atolls of the Pacific. Notwithstanding the testimony of Captain Beechey and others about occasional catastrophes (which are mostly catastrophes to the islets and banks within the lagoons), I was led to look upon a coral-island as one of the most stable of structures. The waves and currents have shaped its reef, shore-platform, and beaches, fitting it well in all respects for its place by means of the forces that were to assail it; and an air of placid repose, as it lies amid the breakers, is its most impressive feature. Through the wind-made and tidal movements the loose sands are drifted along the shores and over the reef; edges of the reef are broken off in gales or by earthquake waves; and occasionally a mushroom islet in the lagoon, where growing corals are not compacted by wave-action, is overthrown by the same means; but beyond this the structure is singularly defiant of the encroaching waters. Earthquakes may bring devastation; and so they may to other lands.

* Address, p. 23.

VI. *Conclusion.*

With the theory of abrasion and solution incompetent, all the hypotheses of objectors to Darwin's theory are alike weak ; for all have made these processes their chief reliance, whether appealing to a calcareous, or volcanic, or mountain-peak basement for the structure. The subsidence which the Darwinian theory requires has not been opposed by the mention of any fact at variance wth it, nor by setting aside Darwin's arguments in its favour ; and it has found new support in the facts from the 'Challenger's' soundings off Tahiti that had been put in array against it, and strong corroboration in the facts from the West Indies.

Darwin's theory therefore remains as the theory that accounts for the origin of coral reefs and islands.

VII. *Central-Pacific Subsidence.*

Darwin, as has been said, took a step beyond direct observation in his inference that the subsidence attested to by each atoll extended over the intermediate seas and characterized a large central area of the ocean. He may be wrong here (and the writer with him), while not wrong in his theory. But, considering the distribution of the Pacific atolls in the ocean, their relation in this respect to the distribution of other Pacific lands, and the facts connected with the history of coral reefs and islands, the generalization appears to be well sustained. The question is here left without further argument, to be considered over the best geographical map of the ocean to be had, and the best bathymetrical map that can be made, only asking that the doubts which physical theory has set afloat may not be allowed by the geologist to warp the judgment or cripple investigation*.

My own agreement with Darwin as to the area of coral-reef subsidence was promoted by an early personal study of the oceanic lands. For more than five years previous to passing my third decade I was ranging over the oceans, receiving impressions from a survey of the earth's features. I was

---

* One point often encountering an *à priori* doubt is the slowness of the required subsidence. The subsidence over the Appalachian region which preceded the making of the Appalachian Mountains amounted, according to well-ascertained facts (as stated by Hall and Leslie), to at least 30,000 feet. The great trough, nearly a thousand miles long, was in progress through all of Palæozoic time. If the Palæozoic ages covered only 20,000,000 years (a low estimate) the mean annual rate was 0·018 inch, which is less than half a millimetre per year. Such a fact is no evidence as to the rate of the atoll-making subsidence; but, whatever the cause to which the Appalachian subsidence is to be attributed, it is suggestive as to possibilities and probabilities connected with the earth's movements.

made to see a system of arrangement in the Pacific islands, instead of a " labyrinth ;" to appreciate the vast length of the island-chains in the great ocean with their many parallelisms, and the accordant relations subsisting between them and long lines of atolls. I was thence led to observe the corresponding system in the features of the continental lands, and the more fully so when afterwards it was proved that Geology was not in America merely the study of strata and fossils, but of the successive stages in a growing continent.   Thus a conception of the earth as a unit became early implanted, and the idea also of its development as a unit under movements as comprehensive as the system in its feature-lines.   My faith in any mountain-making theory hitherto proposed is weak.   But that idea of system in structure and progress stands, and, however much ignored by students of the earth's stratigraphy, it must have its explanation in a true theory of the earth's dynamics.

XXX. *On an unnoticed Danger in certain Apparatus for Distribution of Electricity. By* J. HOPKINSON, *F.R.S.*[*]

MANY plans have been proposed, and several have been to a greater or less extent practically used, for combining the advantage of economy arising from a high potential in the conductors which convey the electric current from the place where it is generated with the advantages of a low potential at the various points where the electricity is used. A low potential is necessary where the electricity is used ; partly because the lamps, whether arc or incandescent, each require a low potential, and partly because a high potential may easily become dangerous to life. Amongst the plans which have been tried for locally transforming a supply of high potential to a lower and safer, the most promising is by the use of secondary generators or induction-coils. It has been proved that this method can be used with great economy of electric power and with convenience ; under proper construction of the induction-coils it may also be perfectly safe. It is, however, easy and very natural so to construct them that they shall be good in all other respects but that of safety to life—that they shall introduce an unexpected risk to those using the supply.

In a distribution of electricity by secondary generators, an alternating current is led in succession through the primary coils of a series of induction-coils, one for each group or system of lamps.   The lamps connect the two terminals of the

secondary coil of the induction-coils. It is easy to so construct the induction-coils that the difference of potential between the terminals of the secondary coils may be any suitable number of volts, such as 50 or 100 ; whilst the potential of the primary circuit, as measured between the terminals of the dynamo machine, may be very great, *e. g.* 2000 or 3000 volts. If the electromagnetic action between the primary and secondary coils, on which the useful effect of the arrangement depends, were the only action, the supply would be perfectly safe to the user so long as apparatus with which he could not interfere was in proper order. But the electromagnetic action is not the only one. Theoretically speaking, every induction-coil is also a condenser, and the primary coil acts electrostatically as well as electromagnetically upon the secondary coil. This electrostatic action may easily become dangerous if the secondary generator is so constructed that its electrostatic capacity, regarded as a condenser, is other than a very small quantity.
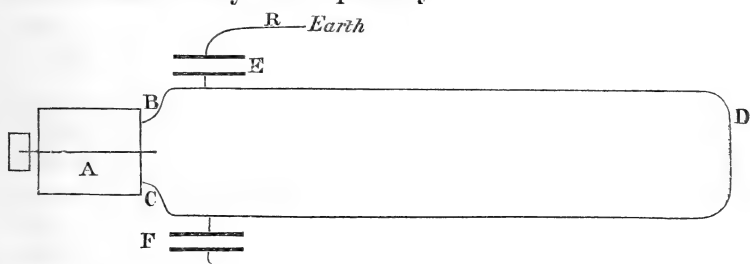
Imagine an alternate-current dynamo machine, A, its terminals, B, C, connected by a continuous conductor, B D C, on which may be resistances, self-induction-coils, secondary generators, or any other appliances ; at any point is a condenser, E, one coating of which is connected to the conductor, or may indeed be part of it, the other is connected to earth through a resistance, R. Let K be the capacity of the condenser, V the potential at time t of the earth-coating of the condenser, U the potential of the other coating, x the current in resistance R to the condenser from the earth, being taken as positive, and the earth-potential as zero. We have

$$x = \frac{V}{R}, \ K(U^{\boldsymbol{\cdot}} - V^{\boldsymbol{\cdot}}) = x ;$$

whence, since

$$U = A \sin 2\pi nt,$$

where A is a constant depending on the circumstances of the dynamo circuit as well as the electromotive force of the machine, and n is the reciprocal of the periodic time of the

machine, we have

$$KR\dot{x} + x = 2\pi nKA \cos 2\pi nt,$$

$$x = \frac{2\pi nKA}{(KR2\pi n)^2 + 1} \{ -2\pi nKR \sin 2\pi nt + \cos 2\pi nt \},$$

mean square of $x = \dfrac{2\pi nK}{\sqrt{(KR2\pi n)^2 + 1}}$. mean square of A.

Let us now consider the actual values likely to occur in practice. Let the condenser E be a secondary generator ; let the resistance R be that of some person touching some part of the secondary circuit, and also making contact to earth with some other part of the body ; n may be anything from 100 to 250, say 150 ; K will depend on the construction of the secondary generator—it may be as high as 0·3 microfarad or even more, but there would be no difficulty even in large instruments in keeping it down to one hundredth of this or less. The mean square of A will depend on the circumstances of other parts of the circuit; it might very easily be as great, or very nearly as great, as the mean difference of potential between the terminals of the machine if the primary circuit were to earth at C. Suppose, however, that the circuit B D C is symmetrical, that E is at one end, and that another person of the same resistance as the person at E is touching the secondary circuit of the secondary generator F at the other end of the circuit. In that case, if 2400 be difference of potential of the machine, mean square of A will be 1200 ; in which case we have, taking R as 2000 ohms,

mean square of $x = \dfrac{2\pi \times 150 \times 0\cdot 3 \times 10^{-6}}{\sqrt{(2\pi \times 150 \times 0\cdot 3 \times 10^{-6} \times 2000)^2 + 1}} \times 1200$

$$= \text{about } 0\cdot 3 \text{ ampere.}$$

Experiments are still wanting to show what current may be considered as certain to kill a man, but it is very doubtful whether any man could stand 0·3 ampere for a sensible length of time. It is probable that if the two persons both took firm hold of the secondary conductors of E and F, both would be killed. If the person at F be replaced by an accidental dead earth on the secondary circuit of F, the person at E would experience a greater current than 0·3 ampere.

It follows from the preceding consideration that secondary generators of large electrostatic capacity are essentially dangerous, even though the insulation of the primary circuit and of the primary coils from the secondary coils is perfect. The moral is—for the constructor, Take care that the secondary generators have not a large electrostatic capacity, say not

more than 0·03 microfarad, better less than $\frac{1}{100}$ microfarad ; for the inspector, Test the system for safety. The test is very easy. Place a secondary generator of greatest capacity at one end of the line and connect its secondary circuit to earth through any instrument suitable for measuring alternate currents under one ampere ; put the other end of the primary to earth ; the reading of the current-measuring instrument should not exceed such a current as it may be demonstrated a man can endure with safety.

XXXI. *On Supersaturation of Salt-Solutions.* *By* W. W. J. NICOL, *M.A., D.Sc., F.R.S., Lecturer on Chemistry, Mason College, Birmingham*[*].

IN my previous paper[†] on this subject I described experiments which proved that a so-called supersaturated solution was able to dissolve more of the salt it already contained, provided only that the salt was added in the dehydrated state, and under conditions which precluded the possibility of access of crystals of the hydrated salt. I also expressed the opinion that a supersaturated solution is merely a solution of the anhydrous salt which may, or may not, be saturated; and that it differs in no way from an ordinary solution so long as no disturbing cause operates to bring about the formation of a hydrate which exists only in the solid state.

Until I made the experiments described in the following paper, I was of the opinion that although a hydrated salt existed in solution in what may be termed an anhydrous state, still, when a dehydrated salt is dissolved in *pure* water, solution always took place in two stages—the first consisting of the hydration of the salt to form the solid hydrate, and that this was followed by solution accompanied by the decomposition of the hydrate thus formed ; but the experiments I am about to describe are, I think, conclusive, and show clearly that solution of the dehydrated salt in *pure* water is unattended by the formation of any hydrate, solid or liquid.

Two similar wide-mouthed bottles, capable of holding some 60 cubic centim. of water, were taken ; in each were placed 25 cubic centim. of the same sample of distilled water, and in each a glass bulb containing 5 grms. of dehydrated Na_2SO_4. One of the bottles (No. 1) was placed at once in the constant-temperature bath at 20° C. ; the other (No. 2) was placed in a water-bath which was raised to the boiling-point ; it was then, after cooling, placed alongside the first bottle. After

some time the two bottles were taken out and shaken, so as to break the bulbs and thus bring the dehydrated Na_2SO_4 in contact with the water. After a few seconds' shaking, the salt was completely dissolved in bottle No. 2, which had been heated ; but the salt in bottle No. 1 had caked into hard masses, which dissolved only very slowly. In this case the solid hydrate was formed ; while in the other, solution had taken place without hydration.

Another experiment with the same quantity of water, but a larger amount (10 grms. of Na_2SO_4 in both bottles), was attended with a like result.

A third experiment, with the same quantities of water and salt as in the previous case, differed to some extent from it. In both bottles solution was complete at once ; but the contents of the bottle which had not been heated crystallized out again in a few seconds.

A fourth experiment gave results identical with the second experiment. In each of these three last experiments the solution in bottle No. 2 was distinctly supersaturated, crystallizing on removing the stopper.

I have made numerous other experiments similar to the above, and have never failed in obtaining a supersaturated solution in this way. I noted that when special care was taken in cleaning the bottles and fresh distilled water was employed, it was frequently the case that the solution behaved as in experiment No. 3 above ; but I shall return to this later.

A saturated solution at 20° of the hydrated salt contains, according to Mulder[*], 19·5 parts of the anhydrous salt per hundred parts of water. Thus, the supersaturated solutions I prepared as above described contained more than twice as much Na_2SO_4 as a saturated solution prepared in the ordinary way. It remained to be seen to what extent this supersaturation may be pushed—in other words, to find the amount of salt in a true saturated solution of Na_2SO_4.

A bottle containing 25 cubic centim. of water and 15 grms. of Na_2SO_4 sealed up in a bulb was treated as above, and after shaking was allowed to remain in the bath at 20° for several hours. The stopper was then removed and some of the clear solution was rapidly poured into a previously weighed platinum dish, and in this way the percentage of salt was obtained. Two trials gave :—

(1)   35·87 per cent., $\rbrace$ corresponding to 55·63 parts
(2)   35·61 per cent., $\rbrace$ per 100 parts of water.

* *Bijdragen tot de geschiedenis van het scheikundig gebonden Water* (Rotterdam, 1864).

Another experiment at 25° gave

$$35 \cdot 63 \text{ per cent.} = 55 \cdot 35 \text{ per } 100.$$

Another pair at 30° C. gave

$$\left.\begin{array}{ll} (1) & 34 \cdot 25, \\ (2) & 34 \cdot 13, \end{array}\right\} = 51 \cdot 94 \text{ per } 100 ;$$

while another at 33° C. gave

$$51 \cdot 09 \text{ per } 100.$$

Before proceeding further I wish specially to lay stress on the approximate nature of the above figures. They are all necessarily high, for two reasons in particular. One is, that it is impossible to filter the solution, for the instant it comes in contact with the air crystallization commences ; thus, as it is very dense and far from mobile, it is impossible to obtain the solution perfectly clear. The second cause that raises the percentage is, that a very considerable evolution of heat accompanies the solidification, and thus some of the water is driven off, even when the dish is covered. In spite of this the figures show clearly enough a decrease in solubility as the temperature rises.

As is well known, the solubility-curve of Na_2SO_4 ascends rapidly to a point about 33° C. (Mulder 32°·75, Kopp 32°·93) and then descends slowly to 100° C., after which it rises again[*]. This change of solubility at 33° C. is usually ascribed to the dissociation of the decahydrate at that temperature ; but I shall return to this. The most reliable data relating to the solubility of Na_2SO_4 are those given by Gay-Lussac[†] and Mulder[‡]. From the results of Gay-Lussac's experiments Kopp[§] constructed the following interpolation-formulæ.

Below 30° C. The quantity dissolved in parts per 100 is

$$\text{(I.)} \quad Q = 5 \cdot 02 + 0 \cdot 30594 \, t - 0 \cdot 00041 \, t^2 + 0 \cdot 0009977 \, t^3.$$

Above 40°,

$$\text{(II.)} \quad Q = 58 \cdot 5 - 0 \cdot 27783 \, t + 0 \cdot 00069 \, t^2 + 0 \cdot 0000049802 \, t^3.$$

And the point of intersection of the two curves is given by

$$-0 \cdot 0009927 \, t^3 + 0 \cdot 0011 \, t^2 - 0 \cdot 58377 \, t + 53 \cdot 48 = 0 ;$$

whence

$$t = 32 \cdot 93.$$

Now the agreement of the figures found by both Gay-Lussac and Mulder with the values calculated by Kopp's formulæ is very complete, as is shown by the table, where Mulder's results are compared with Kopp's figures.

---

[*] *Conf.* Mulder, *loc. cit.* page 120.
[†] *Ann. Chim. et Phys.* [2] xi. p. 312.
[‡] *Loc. cit.* page 123.
[§] *Ann. Chem. und Pharm.* 1840, xxxiv. p. 271.

$t°$.	Mulder.	Kopp.	
100	42·5	42·597	Formula II.
90	43·1	42·717	,,
80	43·7	43·242	,,
70	44·4	44·840	,,
60	45·3	45·391	,,
50	46·7	46·958	,.
40	48·8	48·811	,,
30	40·9	41·135	Formula I.

	Nicol.		
33	51·09	50·263	Formula II.
30	51·94	50·921	,,
25	55·35	52·064	,,
20	55·63	53·260	,,

The lower half of the table compares the results I obtained as described above, compared with the figures obtained from Kopp's second formula extended below 33° C. ; and the concordance here is, I venture to think, thoroughly satisfactory when the difficulties attending such determinations are taken into account. My results will also be found to agree well with those of Loewel[*], who determined the solubility at 20°, and 25°, and 30° of the anhydrous salt by heating an excess of the decahydrate and water above 33°, and then allowing the solution thus obtained to cool in contact with the separated anhydrous salt.

These experiments conclusively prove the truth of my contention, that a so-called supersaturated solution differs in no way whatever from an ordinary solution. The arguments advanced in the previous paper on this subject were incomplete in one point. They left room for the objection that a solution of sodium sulphate might, for all we know, have a different constitution, after heating and cooling, from that possessed by a similar solution that has not been heated. To such a change of constitution has been ascribed the possibility of the existence of supersaturated solutions; but now that supersaturated solutions have been prepared from cold water and cold dehydrated Na_2SO_4, and have been found precisely similar to those prepared with the aid of heat, this theory falls to the ground, and there is no reason for regarding them as anything but ordinary solutions of the anhydrous salt.

Why, then, do these solutions crystallize when brought in contact with the air? or why is it that they cannot be pre-

[*] *Ann. de Chim. et Phys.* [3] xlix.

pared from water and dehydrated salt without heating these out of contact with the air? and what effect has this heating?

There is no doubt that one, if not the sole, cause which brings about crystallization of a supersaturated solution is the presence of a crystal of the hydrated salt; and it is for this reason that supersaturated solutions can exist only out of contact with the air of the laboratory. This also is the reason that the water and anhydrous salt must be heated before they are brought in contact; for minute crystals of the solid hydrate may lie hid in the scratches in the neck of the bottle or in the mass of dehydrated salt, and these must be heated above 33° before they are decomposed, and so lose their power of determining the union of the dehydrated salt and the water with which it is brought in contact. The fact that no hydration of the salt takes place *before* solution is conclusively proved, not only by the formation of a supersaturated solution which cannot exist in the presence of undissolved hydrate, but also by the fact that the finely powdered dehydrated salt dissolves at once; or if excess be present, the portion remaining undissolved retains its powdery form, no caking together or change in appearance taking place.

Finally, a very considerable *rise of temperature* attends the solution of the salt quite equal to—so far as it is possible to judge without quantitative determination of its amount—if not actually greater than, that attending the solution of the dehydrated salt under ordinary conditions. Now, as shown above, there is no hydration, and the question remains—To what is this change of temperature due? This cannot be fully answered until our knowledge of the volume and temperature changes attending the solution of the dehydrated salt is more complete than at present. The probable explanation however is, I venture to suggest, to be found in the great contraction attending the act of solution. According to the most reliable determinations, the density of Na_2SO_4 (solid) is 2·6618 at 20° C. This gives the molecular volume 53·35. But, as shown in my previous paper, the molecular volume of Na_2SO_4 (dissolved) in a solution containing 6·244 molecules of salt (that is, 49·26 per 100) is 32·79. A saturated solution, as shown above, contains not more than 55·6 per 100, and the molecular volume in such a solution cannot exceed 33·5. The contraction, then, attending the solution of one gramme-molecule of Na_2SO_4 is 53·4 − 33·5 = 19·9, or nearly 20 cubic centim., or about 40 per cent.; a quantity possibly sufficient to account for the thermal change, exceeding, as it does, the volume-change on solution of other anhydrous salts, which dissolve with either a slight rise or fall of temperature. For a further extension of this argument reference must be made to the papers of Müller-

Erzbach[*], who has done much to extend our knowledge of the connection between stability of compounds on the one hand, and, on the other, the volume and thermal changes attending their formation.

XXXII. *Notices respecting New Books.*

Textbook of Practical Physics. *By* R. T. Glazebrook, *M.A., F.R.S., and* W. N. Shaw, *M.A.* London: Longmans, Green, and Co. (482 pp.).

THE development of practical work as a necessary part of the teaching of science in its various branches is a very healthy sign of the times, and promises well for the advantages we may expect from the increased study of science which has marked the last twenty years. Formerly such things as laboratories for the practical study of Biology, Physics, &c. were almost unknown in England, except in a few of the more advanced educational institutions, and Chemistry was apparently the only science thought worthy of being studied practically. Now there are numerous well-equipped laboratories for the practical study of Physics; and it is for the use of teachers and students in such that this book is intended, and it will be welcomed by all teachers of the subject as supplying a much felt want. The Authors, in marking out the limits of their work, had to decide between attempting to give instructions equally applicable to all the different forms of instruments to be met with in different laboratories, which must of necessity have been very vague, and adhering to the descriptions of the precise instruments in use in their own laboratory; and have decided, we think very wisely, in adopting the latter course, trusting that the necessity for adaptation to corresponding instruments used elsewhere will not seriously impair the usefulness of the book. Their general aim has been to place before the reader a description of a course of experiments which shall not only enable him to obtain a practical acquaintance with methods of measurement, but also, as far as possible, illustrate the more important principles of the various subjects. There are two valuable introductory chapters—one on the units employed and their dimensions, the other on the arithmetic of numbers expressing *approximate* measurements. We may quote, as an example, the application of the principles of this chapter to find the effect on the value of a current, as deduced from observations with the tangent-galvanometer, of an error of a quarter of a degree in the reading.

The formula of reduction is

$$C = k \tan \theta.$$

Suppose an error δ has been made in the reading of θ, so that the observed value is

$$C' = k \tan (\theta + \delta).$$

It is shown that when δ is less than a certain small value, this is

---

[*] Pogg. *Ann., Berichte,* Wied. *Ann.,* Lieb. *Ann.,* 1870–85. Summarized in Meyer, *Mod. Theor. d. Chem.* p. 445.

equal to $k (\tan \theta + \delta \sec^2 \theta)$; hence

$$C' - C = k\delta \sec^2 \theta,$$

and

$$\frac{C' - C}{C} = \frac{k\delta \sec^2 \theta}{k \tan \theta} = \frac{\delta}{\sin \theta \cos \theta} = \frac{2\delta}{\sin 2\theta}.$$

The error δ must be expressed in circular measure; if it be equivalent to a quarter of a degree, we have

$$\delta = \frac{\pi}{4 \times 180} = 0 \cdot 00436;$$

$$\therefore \frac{C' - C}{C} = \frac{\cdot 00872}{\sin 2\theta}.$$

Hence we see, not only that when θ is known the effect of the error can be calculated, but also that the effect of a given error is least when the deflection is 45°.

The different forms of balance, determinations of specific gravity, and the mechanics of solids, liquids, and gases occupy 110 pages; various experiments connected with sound, 16 pages; the thermometer, determinations of expansion, specific and latent heat, and hygrometry, 58 pages; experiments with light, 100 pages; and the rest of the book (130 pages) is taken up with magnetism, electricity, and electromagnetism. The theories of the balance and thermometer are given with unusual completeness; and the chapter on hygrometry forms a complete elementary treatise upon the subject. But perhaps the most important part of the book is that which relates to electricity, in which full and clear instructions are given for the comparison and measurement of currents, resistances, and electromotive forces, capacities of condensers, and so on. It should be noticed that the book is well up to date. Thus, for example, we have, in the description of Carey Foster's method of employing the B.A. form of Wheatstone bridge, an account of Dr. Fleming's form of bridge, described in the Proceedings of the Physical Society, and in this Magazine for May 1884.

The sincere thanks of all teachers and students of Physics are due to the Authors for their valuable book.

XXXIII. *Intelligence and Miscellaneous Articles.*

ON THE ELECTRICAL RESISTANCE OF ALCOHOL.
BY M. G. FOUSSEREAU.

I EXAMINED the specific resistances of alcohol, and its mixture with water and with salts, by comparing them with the known resistance of a pencil-mark drawn on a plate of ebonite. I used M. Lippmann's method, and the experimental arrangement which I employed in several previous researches[*]. Different specimens of the absolute alcohol of commerce gave, at the temperature 15°, specific resistances comprised between 2·47 and 3·68 megohms. These differences may, *à priori*, be ascribed either to the presence of a

[*] *Comptes Rendus*, May 26 and July 15, 1884.

trace of water, or to the solution of substances from the sides of the receiver.

In order to estimate the degree of influence of these various causes, I first added to specimens of the same alcohol increasing weights of distilled water, the resistance of which was nearly ten times less than that of the alcohol used. I ascertained that the resistance of the mixtures thus obtained goes on decreasing, and attains a maximum which does not much differ from the resistance of water, when there is not more than 3 per cent. of water, and then increases up to the resistance of water. But a notable alteration of composition is always necessary to produce a distinct change in the resistance of the mixture. The difference between the numbers cited above cannot therefore be ascribed to the small quantity of water which commercial absolute alcohol might retain.

If, on the contrary, a trace of a standard solution of chloride of sodium is added, an enormous alteration is produced in the resistances. A fall in the ratio of $1 : 0\cdot527$ is obtained by the addition of a weight of salt representing $\frac{1}{2,600,000}$ that of alcohol. We are thus led to attribute the variations to the absorption by the alcohol of some ten millionths of salts from the vessel which contains it.

I have, in fact, observed that the conductivity of alcohol increases in glass vessels more rapidly than that of water. It may double in a few hours. Absolute alcohol prepared with great care and kept for two years in a closed and full glass vessel in the chemical laboratory of the Ecole Normale was ten times as good a conductor as commercial absolute alcohol. Burnt upon a platinum plate, this alcohol coloured the flame yellow. It contained a trace of soda salts from the glass.

I endeavoured to avoid these alterations by dispensing with the use of glass vessels ; and with this view I had absolute alcohol collected in porcelain vessels in the manufactory of M. Billault. I have observed the resistance to increase, and for the specimens in question to $5\cdot14$ and $5\cdot44$ megohms at $15°$. The second specimen, contained in biscuit porcelain, retained a remarkable constancy for several days.

M. Delachanal was kind enough to prepare for me, by a series of distillations, alcohol at its minimum density like that which is used for determining the point 100 of the new alcoholometers. Two specimens of this were sent to me, one in a porcelain and the other in a glass vessel. The former gave at $15°$ the resistance $7\cdot031$ megohms, the greatest I have observed ; the other, which was already altered by the glass, was $2\cdot823$ megohms. A fresh specimen, prepared in the same way six days after the first and kept in a porcelain vessel, gave $6\cdot899$ megohms, only differing from the other by $\frac{1}{56}$ of the value. Although traces of dissolved salts cannot appreciably alter the density of alcohol, it might be desirable to distil and preserve in porcelain receptacles the alcohol intended for delicate chemical operations.

I have also examined the changes which alcohol experiences when its temperature varies. I found that the resistance diminishes in the mean by $0\cdot0145$ of its value, when the temperature is

raised through one degree, near the ordinary temperatures. This variation is not proportional to that of the coefficient of internal friction, as is the case with distilled water; and for salts this latter quantity varies, in fact, $0 \cdot 0210$ of a degree at the same temperature. The mechanism of conductivity is therefore more complex for alcohol than for salts and their aqueous solution.

This research was made in the Laboratory for Physical Research at the Sorbonne.—*Comptes Rendus,* July 20, 1885.

THE VOLCANIC NATURE OF A PACIFIC ISLAND NOT AN ARGUMENT FOR LITTLE OR NO SUBSIDENCE. BY J. D. DANA[*].

In the remarks on this point in § 13 (Part I.) of my paper on the Origin of Coral Reefs and Islands, I refer to the great depths found in the ocean by soundings in the vicinity of Hawaii, and speak of the facts as favouring the idea of more subsidence about that south-eastern end of the group than along the north-western, although the latter is the coral-island end. Another example of similar character, but more striking, is afforded by the region of the Ladrones. This north-and-south range of islands has its largest volcanic islands in the southern part, and dwindles in the opposite direction to islands which are little more than tufa cones[†]; and 200 miles south of Guam, the largest island, the 'Challenger' found a depth of 4475 fathoms (26,850 feet), one of the deepest regions of the ocean. It hence may be that Guam, like Hawaii, is a large island, not because of small subsidence, but because of continued eruptions that made it large in spite of the sinking that was in progress. The question arises how far the depths in these particular cases are due to the undermining effects of volcanic eruption. There are coral islands both north-east of the deep region, near Guam, and also of large size, to the south-west and south-east, not three degrees off; the former, those of an extension of the Pelew range, and the latter, islands of the Caroline archipelago.

ON THE QUANTITY OF ELECTRICAL ELEMENTARY PARTICLES. BY E. BUDDE.

There exists an attempt by Herwig[‡] to estimate the magnitude of electrical elementary particles; which, however, is open to the objection of making some very arbitrary assumptions, and moreover of confounding the ideas of "mass" and "quantity" of particles. I believe that the following simple considerations lead to a tolerably certain result for the quantity of electrical "atoms."

In the sphere of ponderable masses we find that a definite body, such as carbon, always enters into combination with a definite relative weight, twelve. From this and from similar observations with all other masses we conclude that carbon consists of atoms, and that each of its atoms has the relative weight twelve. If we

---

[*] Communicated by the Author.

[†] One of the two northern (Assumption Island) I give the outline of on page 354 of my Expedition Geological Report.

[‡] Pogg. *Ann.* vol. cl. p. 381 (1873).

were in a position to deal with separate atoms, experiment would not only refer to the relative weight of carbon atoms, but we should see that carbon enters into all combinations with multiples of a definite absolute weight; the above conclusions would then shape themselves more definitely, and experiment would directly teach us the absolute value of the atomic weight of carbon.

We propose to ourselves the questions, (1) Are there in nature discrete elementary particles of electricity? (2) What is their magnitude? According to the analogy of the conclusions just drawn for carbon, this question may be answered as follows:—If there are in nature discrete elementary particles of electricity, it is to be expected that an absolutely definite, very small quantity of electricity occurs, and plays an important part in a large number of processes. If experiment shows us such an amount, then that amount of electricity is the probable quantity of the particles of electricity. The region in which we must investigate, is that of those processes in which electricity interacts with ponderable atoms, and defines the action of those ponderable atoms—that is to say, the region of electrolytical decompositions and combinations.

Here we meet with Faraday's law, which, referred to individual atoms, may be expressed as follows:—

Let KA be an electrolyte, which is separated by the voltaic current into the parts K and A, of which each has the valency n; let q be the quantity of positive electricity which goes with each separate atom or radical K to the kathode; q/n *is then for all bodies and for all currents the same absolutely definite magnitude.*

On the basis of the above we may also say: q/n is the absolute quantity of an elementary particle of electricity with the same probability with which twelve is the relative atomic weight of carbon.

q/n can be easily calculated. Let h be the magnetic intensity of that current which in unit time liberates a milligramme of hydrogen, ch its intensity in mechanical measure, N the number of molecules of hydrogen in a milligramme; the milligramme contains then 2N atoms, and these bring the quantity $ch/2$ of positive electricity to the kathode, by which $n=1$. Hence the quantity which is attached to an atom is

$$E = \frac{ch}{4N}.$$

In this we have approximately[*] in mm., mg., sec., $c = 3 \cdot 10^{11}, h = 957$; and further, according to the theory of gases, $N = 14 \cdot 10^{19}$. This gives
$$E = 0 \cdot 00000051 \text{ mg.}^{\frac{1}{2}} \text{ mm.}^{\frac{3}{2}} \text{ sec.}^{-1}.$$

This value is thus the probable "Atomic quantity of Electricity." It may be a multiple, but with the same probability with which $C = 12$, and not 6, or 3, is E the quantity of electrical elementary particles. For even if electricity can be split into smaller parts than E, it is not clear why such a smaller part is never met with in experiment.—*Wiedemann's Annalen*, No. 8, 1885.

* *Conf.* Wiedemann, *Galvanismus*, iii. p. 450; and O. E. Meyer, *Kinetische Theorie der Gase* (Breslau, 1877), p. 234.

XXXIV. *On the Electric Conductivity of Gases.*
By F. Stenger*.

[Plate IX.]

THE present research has two objects. In the first part, the author endeavours to show, partly by use of the unusually rich literature of the subject, and partly from his own researches, that there exists no distinction universally applicable between the arc-discharge and the glow-discharge.

Upon what factor the appearance of the one or other of the two forms depends, and under what experimental conditions the two forms of discharge can pass into each other, will form the subject of the second part.

PART I.

I may be allowed, in the first place, briefly to place together the essential characters of the arc-discharge as distinguished from the glow-discharge ; and for this purpose I confine myself entirely to the normal form of discharge.

(1) The gas-stratum in the arc-discharge possesses a much smaller resistance than in the glow-discharge.

(2) In the arc-light the anode is more strongly heated than the kathode, whereas in the glow-light the reverse is the case.

(3) In the spectrum of the arc-light, the light due to the substance of the electrodes overpowers that of the stratum of gas between them ; while, on the other hand, in the glow-dis-

charge the spectrum shows only the lines of the stratum of gas, and the nature of the electrodes is a matter of indifference.

(4) In the arc both electrodes become disintegrated although in different degree, whilst with the glow-discharge disintegration takes place only at the kathode.

§ 1. *On the Resistance of the Stratum of Gas.*—With the glow-discharge in exhausted gases it is, according to Hittorf [*], the first two layers of the kathode-light which oppose resistance to the passage of the electric current, in comparison with which the resistance of the positive brush-discharge is very small.

Since, as the pressure decreases, both layers continually expand, the resistance of the kathode-light increases simultaneously. When Hittorf passed, on the other hand, to higher pressures of gas, the thickness of the glow-light decreased and the strength of current increased. With a vacuum-tube filled with nitrogen of about 17 millim. pressure, there appeared, as with high exhaustion, as soon as the circuit was completed, a glow-light of 1 millim. thickness upon the kathode of 17 millim. length, which speedily heated the wire to bright redness, which increased to a white heat sufficient to fuse the thick iridium electrode. If the density of the gas was still further increased, the anode also became white hot, and at the pressure of 53 millim. the anode was even hotter than the kathode. At the same time the strength of the current increased continuously up to 2 amperes, a current-strength not greatly different from that obtained with the arc-light. Certain other observations of Hittorf [†] and Goldstein [‡], however, show very clearly that if the experimental conditions are favourable, the resistance of the gas in the glow-light is of the same order as in the Davy arc-light.

Hittorf employed as kathode a platinum coil heated by means of a strong current passed through it, and found that the resistance remained unaltered as long as the platinum was only red hot, but that the sudden diminution of resistance occurred as soon as it became white hot, which continued as the temperature of the platinum rose. If the experiment was carried out in the same way with a Carré's carbon-rod, it was possible to obtain a discharge from 10 small elements with the electrodes 4 centims. apart. At a distance of 15 centims., 40 elements gave a constant current of $\frac{1}{10}$ ampere. When Hittorf employed as kathodes the carbons of the Davy arc, the action was much greater. If, on the other hand, the anode

---

* Wied. *Ann.* xxi. p. 97 (1884).   † *Ibid.* xxi. p. 133 (1884).
‡ *Ibid.* xxiv. p. 81 (1885).

was strongly heated, no change in the current-strength could be recognized.

Goldstein has obtained exactly similar results. It appears therefore from these investigations that it is only necessary to employ suitable experimental conditions, in order to obtain with the glow-discharge currents of the same order of magnitude as with the arc-light.

§ 2. Does the temperature of the electrodes in the arc-discharge depend upon the pressure and nature of the surrounding gas?

Gassiot was the first to make observations on the different temperature of the electrodes. A few years later Grove * investigated the behaviour of the arc-light in different gases, and in a vacuum such as could be obtained at that time. His results only partially agree with my observations. According to Grove, the temperature of both electrodes is the same in hydrogen or in nitrogen, or in a tolerably perfect vacuum, judging from the colour and rapidity of cooling. But, as he himself remarks, in an atmosphere of hydrogen he only succeeded with carbon electrodes in maintaining the arc constant for any time, so that his result that then the electrodes show no difference in temperature cannot be considered of any great weight. I have also endeavoured in vain to obtain a constant arc-light between metallic electrodes in an atmosphere of hydrogen. As Liveing and Dewar† have remarked, the length of the arc is much less in hydrogen than in air, and hence a small increase in the distance of the electrodes apart extinguishes the light. But that the temperature of the electrodes may be very greatly different, when the current is closed only for a short time, and when it is maintained burning, appears clearly from the statement of Moigno, that after contact between the electrodes has been broken for production of the arc, first white light flashes out from the point of the negative electrode, and only then does the positive begin to glow. With carbon electrodes, on the other hand, I have established by a series of experiments that in hydrogen, as in nitrogen, the anode always possesses a higher temperature than the kathode, although the difference may not be so marked as in air. There would appear then to be some ground for Grove's suggestion that secondary phenomena play a part in gases which contain oxygen. That in observations of this kind the arc should be maintained for some minutes, before making the comparison of temperatures, appears from the fact that both carbons are often seen to cool simultaneously,

* Phil. Mag. [3] xvi. p. 478 (1840).
† Proc. Roy. Soc. xxx. p. 156 (1880).

when the arc has been interrupted immediately after its establishment. Most of these experiments have been made with an extremely simple form of apparatus, which permits working with pure gases in very various pressures, since the movement of the electrodes can be effected without the use of stoppers, which are never absolutely air-tight. The apparatus (fig. 1) consists of a bulb with two tubes blown on to it ; each of the tubes is further provided with a tube at the side, of which the one communicated with a Bessel-Hagen air-pump and the other with the apparatus for evolving the gas. The ends of the tubes are provided with caps fitted by grinding, carrying the electrodes, and the electrodes may be brought into contact and separated again, so to form the arc, by simply turning these caps.

This arrangement, however, could not be used for experiments with an arc of greater length. In these cases I have employed another arrangement, represented in fig. 2 in simple form. A tube (*b*) 1 centim. wide and 80 centim. long, was melted on to the centre bulb-shaped part *a*, and communicated by means of an india-rubber tube with a second tube *b'* of similar dimensions. The short side-tube *c* communicated with the mercury-pump. At the top a short tube *d*, also 1 centim. wide but 10 centim. long, was melted on, upon which a wide tube *e* was placed, from which lastly a tube *f*, 80 centims. long, led downwards and was connected with another (*g*) by means of an india-rubber tube. One of the two electrodes (the apparatus was used only with carbon points) was inserted in the tube *d*, so that its end reached to the middle of the bulb-shaped portion, and was held in position by means of four copper bars, attached to a copper ring which was clamped close to the carbon. The wide tube *e* was then melted together at the top. The current was conducted to the upper carbon by means of mercury which filled the system of tubes *f*, *g* and the space between *c* and *d*, and surrounded the four copper wires. The lower carbon floated on mercury in the tube *b*, so that the distance between the carbons could be altered by simply raising or lowering *b'*.

It appeared to me of importance by means of this apparatus to control the statement of Grove, that in a vacuum the two carbons show no difference or very little difference in temperature. For this purpose air, which had been repeatedly and carefully dried, was introduced into the apparatus and exhausted by means of the air-pump to a pressure of less than $\frac{1}{10}$ millim. As soon as the current of the Gramme machine had established the arc-light, a considerable increase of pressure took place in consequence of evolution of gas from the glowing carbons.

The level of mercury in the communicating tubes b b' consequently sank, and the distance of the electrodes increased considerably, often up to 2 centims., without extinguishing the light. On the contrary, the light was remarkably steady. The temperature of the carbons was then only a little different, but the difference could be recognized with certainty, and upon interruption of the current the kathode ceased to glow somewhat sooner than the anode. When the arc had been several times restored, the apparatus being each time exhausted as much as possible, the evolution of gas gradually decreased ; and when at last no further increase in pressure could be perceived, the difference in temperature between the carbons disappeared at the same moment. But since the slow disintegration of the electrodes continually exposes new portions to ignition, I have not succeeded in obtaining pressures under 1 to 2 millim., so that it remains undetermined whether at still lower pressures the kathode would be more strongly ignited than the anode.

In the usual forms of glow-discharge it is always observed that the kathode becomes red or even white hot, while the anode remains dark. That, however, forms of glow-discharge exist in which the temperature of the anode is higher than that of the kathode appears from the experiments of Hittorf described in the first paragraph.

§ 3. *The Spectrum of the Arc and of the Carbons.*—If we observe the spectrum of the arc-light as it is formed in atmospheric air of ordinary pressure, it appears continuous, except that we occasionally see a few metallic lines appear. But at the moment that the current is interrupted, a very large number of bright lines blaze up, which have their origin in the mineral impurities of the carbon. Spectroscopic observations of the carbon-light are made more conveniently by producing the arc *in vacuo*, and with comparatively feeble currents ; we have then at once the advantage that the distance between the carbons may be increased to 1 centim. without the arc becoming broken, and that consequently the spectrum of the kathode, anode, and arc can be easily observed separately. But the main advantage is that the extraordinarily intense continuous spectrum of the particles of carbon which exist in the arc at a brilliant white heat, does not then obliterate the bright lines of the metallic vapours present in the arc.

It has always been supposed that the gaseous atmosphere in which the arc-light is produced is without influence upon the spectrum of the arc ; Liveing and Dewar * first observed

* Proc. Roy. Soc. vol. xxxv. p. 75 (1883).

the lines C and F in the arc produced by the alternating current of a De Meritens machine in an atmosphere of hydrogen ; but with the continuous current of a Siemens machine, on the other hand, only the line C was observed at the moment of interrupting the current, and the F line not even then distinctly. The reason of this behaviour is to be found only in the overpowering brilliancy of the spectrum of the white-hot particles of carbon ; for in my experiments *in vacuo* the hydrogen lines as well as the metallic lines stood out extraordinarily sharply from the bright background of the arc just the same, whether the apparatus had been filled with hydrogen or with dry air. If, on the other hand, we observe the light emitted by the electrodes themselves, the phenomena are essentially different according to circumstances. I will endeavour briefly to describe the process. If the carbons had been already in use for some time, so that the small quantities of gas set free from them by the high temperature no longer produced any rapid change in the pressure, the image of the arc of light was thrown by an assistant upon the slit of the collimator of the telescope by the aid of an achromatic lens, and the light from the upper or under carbon was cut off from the slit by means of a suitable screen. If the current used was weak, the spectrum of the carbon was feeble, and showed at first no bright lines ; after a short time, however, the hydrogen lines as well as a number of metallic lines became sharply visible, first on the one carbon and then on the other. The cause of these sudden changes is to be sought, no doubt, in the fact that the arc does not burn uniformly round both carbons, so that the parts of the carbon points turned towards the collimator at times glow intensely, at times are only feebly luminous. If the current is strong, the spectrum of the carbons is a continuous one.

It results from the observations described that hydrogen is set free at both carbons ; we thus obtain a confirmation of the conclusion that the carbons employed for electric lighting always contain hydrocarbons, which the high temperature of the arc decomposes, partially at least. The investigations of Dewar * have shown that it is impossible to free carbon from hydrogen compounds, even by lengthened heating in a current of chlorine. We are altogether ignorant what composition these compounds may have, or what changes they may suffer, at the high temperature of the arc, except that there is no doubt of the formation of acetylene in the arc in hydrogen, as shown by Berthelot. But whether in this case we have really

* Proc. Roy. Soc. xxx. p. 87 (1880).

to do with a synthesis of carbon and hydrogen to C_2H_2, or whether acetylene is not also formed in a vacuum, and consequently we have to imagine a partial decomposition of the hydrocarbons present in the carbons, appears still uncertain.

§ 4. *The Disintegration of the Electrodes.*—Under the usual conditions of research the process of disintegration produced by the glow-discharge is confined to the kathode ; as far as this extends the glass wall of the vacuum tube is covered with an extraordinarily thin reflecting deposit, which forms very quickly when thin platinum wires are used. The surface of the electrode after some use is found to be eaten away into fine points and hairs, as is seen most distinctly with the difficultly volatile aluminium.

But when Hittorf sent the current of his battery without interposed resistances through a vacuum-tube filled with hydrogen or nitrogen at about 50 millim. pressure, both iridium electrodes became white-hot, and even began to melt ; at the same time the glow-light disappeared from the kathode, and with it the metallic deposit. Hence it appears to me that we must ascribe the metallic mirror formed in normal cases, not to a superficial volatilization produced by the high temperature of the glow-light, but to some peculiar action of the glow-light. An observation of Dewar's would seem to show the same thing, that a metallic deposit formed with magnesium electrodes disappeared again some time after the interruption of the current ; possibly the gaseous molecules, whilst conveying the glow-discharge, possess greater affinities, and form compounds with the metal of which the kathode consists, which under favourable conditions are again gradually absorbed by the electrode. Warren De La Rue and H. Müller obtained a similar result with palladium electrodes in hydrogen-tubes. Under the experimental conditions, however, where both electrodes are heated to intense white heat and even to the melting-point, both emit metallic vapours, as occurs in a greater degree in the arc-light between metallic electrodes.

That with this latter mode of discharge the volatilization of the electrodes takes place as well in air as in other cases and *in vacuo* has long been known. The high temperature of the electrodes is the chief cause of their wasting away, and the loss is only secondarily due to combustion. In air, in consequence of this higher temperature the anode is used up more rapidly than the kathode ; and, further, the electrodes become disintegrated so much the more rapidly the more volatile they are.

The process is somewhat more complicated with the carbon light. With very powerful currents (400 to 500 Bunsen

elements) according to Despretz *, the carbon of the electrodes is changed into vapour, and on the surface of the carbon are seen certain round globules molten together. With feebler currents, such as are generally employed for electric lighting, there can be no possibility of the volatilization of the electrodes. As already remarked, all these carbons contain hydrocarbons ; at the high temperature these become decomposed and leave the electrode as a porous mass of carbon, which gradually crumbles away. In my apparatus (fig. 2) accordingly I found numerous carbon particles imbedded in the fine deposit on the glass walls, which easily dissolved in nitric acid, and must therefore have consisted of compounds of carbon, and not of carbon itself.

Since, further, in a vacuum no difference of temperature between the electrodes could be detected, the waste becomes equal from both, disregarding, of course, differences in the porosity and composition of the carbons.

Collecting, then, the results so far obtained, we see that *there exists no certain criterion by which to distinguish a given discharge as glow-discharge or arc-discharge*, but these very different typical forms pass insensibly into each other.

Before passing from this first part to the intimately connected considerations of the second, I wish to mention in § 5 an observation, which appears to me to be not without interest.

§ 5. *On Changes of Pressure in the Arc-light.*—According to Warren De La Rue and H. Müller †, an increase of pressure occurs in the arc-light upon completing the circuit, which disappears immediately upon interrupting the current.

According to their data the increase of pressure at an initial pressure of $1\frac{1}{2}$ to 28 millim. amounted to from 25 to 50 per cent. Nevertheless some doubt remains as to the existence of the phenomenon, since the experiments ‡ hardly leave it doubtful that the authors did not work with a normal arc-light. By accident I made an observation which seems to show in fact that the discharge produced a momentary increase in pressure. I had led hydrogen into the apparatus shown in fig. 4, so that the pressure amounted to about 50 millim. : as soon as, by raising the mercury, contact between the carbons had been established and the arc had been formed, the level of mercury sank, and with it the lower carbon, until the length of the arc amounted to 3 centim. Fig. 3 may represent the appearance of the arc at this length. The

* *Comptes Rendus*, xxviii. p. 757 (1849); xxix. pp. 48 & 709 (1849).
† See Goldstein's criticism in *Fortsch. der Physik*, 1880, p. 858.
‡ Phil. Trans. clxxi. p. 65 (1879) ; Proc. Roy. Soc. xxix. p. 286 (1879).

centre is surrounded by a helmet-shaped strongly luminous envelope, about which again is a less luminous layer. Then suddenly the lower carbon rose, and came into contact with the upper one, and the process began anew. This occurred some 50 times in a minute. Evidently an increase of pressure occurred which increased the distance between the carbons, so that the arc was extinguished ; but immediately the pressure returned to its former magnitude, and the carbons came into contact again.

This phenomenon would be very well explained by the hypothesis of A. Schuster [*], according to which the process of electric discharge in gases is accomplished by the dissociation of the molecules, but that as soon as the current is interrupted the old condition of the gas is restored.

Part II.

The final result of the first part of our investigation was that the arc-discharge and glow-discharge cannot be sharply distinguished, and that in particular the usually enormous difference in the resistance of the layer of gas does not always exist. In this second part I shall endeavour to show upon what conditions the different magnitude of resistance depends, and that the same cause is at work in all cases of gaseous discharge in which the resistance of the gas is small. It will be the more convenient at once to state my view, and then to show that it is correct in particular cases (§ 6–11).

When in gaseous discharge the resistance of the gas is small, hot metallic vapours are present which conduct the current.

§ 6. I would first of all recall certain experiments which show that incandescent metallic vapours conduct infinitely better than nitrogen, hydrogen, or air.

De La Rue [†] employed for this purpose a globe-shaped vessel with four tubulatures ; two opposite each other served as electrodes of an induction-coil, and the two others for the production of the arc ; the pressure of the nitrogen amounted to from 2 to 3 millim.

A galvanometer included in the induction-circuit served to measure the current-strength, before the voltaic arc was formed. Then the arc-light was produced, and the new current-strength read off.

The result obtained was a great increase in the conducting power, when the arc passed between silver and copper electrodes ; the change was less with aluminium electrodes, and

---

[*] Proc. Roy. Soc. xxxvii. p. 317 (1884).
[†] Phil. Mag. iv. pp. 29, 553 (1865); *Comptes Rendus*, lx. p. 1002 (1865).

feeblest with zinc, cadmium, or magnesium poles. The increase in conductivity was very remarkable with carbon poles. On the other hand, iron and platinum electrodes gave no perceptible difference ; whence it results that the increase in conductivity in the other cases cannot be brought about by the high temperature of the nitrogen. The experiment is, however, so far unfavourable, and allows no conclusion to be drawn as to the true conductivity of the different metallic vapours, since, as Hittorf's work sufficiently proves, the chief resistance of the glow-discharge occurs in the neighbourhood of the kathode ; and with the great distance between the electrodes in De La Rue's experiment, the formation of metallic vapours takes place exclusively in the neighbourhood of the positive brush-discharge.

Moreover, it is to be remembered that in an experimental arrangement of this kind we have to consider, not only what metallic vapours are present, but without doubt also their quantity, that a less volatile metal may therefore afford better conduction than a more volatile one, although the true conductivity, in the first case, may be far worse than in the second.

As a second proof of the relatively good conducting-power of two metallic vapours, I may quote certain observations of Hittorf's * :—" At the temperatures of our flames, at which the gases of which they consist possess so considerable an electric resistance, other vapours have a much greater conductivity. Of all gases, the vapour of potassium conducts best. Next comes sodium. The other metals, so far as they are volatile under these conditions, produce, in the state of gas, little change in the deflection."

Hittorf shows in another place that mercury vapour, in the non-luminous Bunsen flame, conducts much worse than potassium vapour.

That most metals in the Bunsen burner produce no perceptible change in the resistance, is no doubt explained by the fact that the temperature is too low for a sufficient evolution of vapour.

After these preliminary remarks, I will now pass on to consider, in the particular cases where a stratum of gas possesses a relatively small resistance, whether incandescent gaseous vapours are present, and to show their influence.

§ 7. As far as the arc-light between metallic electrodes is concerned, it is universally known that the colour of the light varies essentially with the nature of the metals employed,

* Pogg. *Ann.* cxxxvi. p. 229 (1869).

and that in the spectrum of the arc the corresponding metallic lines appear sharply.

According to Casselmann* the light-arc is of different length with different metals, and is so much the longer the more volatile these are.

He arranges the metals in the following order:—Potassium, sodium, zinc, mercury, iron, tin, lead, antimony, bismuth, copper, silver, gold, platinum. So that potassium yields the longest arc, and platinum the shortest.

As already remarked, there are essentially two factors to be taken into account—the true conductivity of the vapours, and the quantity in which they are formed ; since further, the conductivity depends in a high degree upon the temperature, it is not to be wondered that Hittorf's experiments in the Bunsen flame, and Casselmann's in the arc-light, have given different results.

§ 8. It is less easy to understand the conditions which obtain in the carbon light. That here also metallic vapours, which are introduced into the arc, increase the conductivity, is of course obvious from the preceding results, and it is not even necessary to refer to the data of Casselmann. Hence we obtain a longer arc between carbons which have been saturated with metallic salts than between carbons as they are found in commerce.

But that metallic compounds are abundantly present also in the carbons which are now so largely used for electric lighting may be easily shown. As is well known, the spectrum of the electric arc shows a multitude of bright lines, which are particularly distinct at the moment of interrupting the current, when the continuous spectrum of the white-hot particles of carbon has faded.

The sodium-line is especially brilliant ; besides which we always observe the lines of calcium, iron, and magnesium. The result is always the same, of whatever manufacture the carbons may be ; and it may perhaps be of interest to compare different opinions as to the preparation of good carbons. According to Carré†, good carbons may be obtained by compressing an intimate mixture of lampblack and powdered coal, and strongly igniting after addition of iron, antimony, or tin, or by boiling the carbons for a long time in a solution of metallic salts. Archereau and Sandain recommend a similar method. Jacquelain ‡ proceeds in an entirely different way, since he endeavours to remove all mineral constituents

* Pogg. *Ann.* lxiii. p. 576 (1844).
† *Comptes Rendus*, lxxxiv. p. 346 (1877).
‡ Pogg. *Ann.* Jubelband, cccxl. (1874).

from the carbon by ignition in a current of chlorine, or treatment with molten potash, or by soaking in hydrofluoric acid. As, however, Liveing and Dewar[*] have shown, these methods are not successful in completely removing iron, magnesium, sodium, and calcium.

§ 9. Whilst electric discharges in air, hydrogen, nitrogen, or carbon dioxide require a large electromotive force, because they have to overcome a very high resistance, it is possible in the presence of good conducting metallic vapours to obtain the arc-discharge with comparatively few elements. Thus Hittorf[†], with cylinders of retort-carbon, the ends of which at a distance of 3 to 4 millim. were brought into a Bunsen flame, in which a bead of potassium-salt was heated, obtained the arc-light with 80 of his elements, without its being necessary to first make contact between the carbons. For this it was of no importance whether both points or only the kathode was surrounded by potassium vapour, because, as with the glow-discharge in exhausted gases, the neighbourhood of the kathode offered a much greater resistance also in the gases of the flame.

Further, Gassiot, employing a battery of 400 Grove's elements, observed that upon making contact, the discharge between balls of carbon or of metal was discontinuous, but very quickly passed into the continuous arc-discharge, evidently because metallic vapours had been formed by the sparks which leapt across, which by their small resistance permitted the establishment of a constant current of great intensity.

Lastly, Herschel's artifice is well known, of producing the arc, not by contact of the electrodes, but by means of a spark allowed to pass between them.

§ 10. I have already had occasion to mention observations of Hittorf[‡], in which he obtained in nitrogen of 53 millim. pressure currents of considerable strength by means of his battery of 1600 elements.

The considerable decrease in the resistance of the stratum of gas, as I have already mentioned, was accompanied by intense white heat of the electrodes, so that here also we may very well regard the abundant formation of metallic vapours as the cause of the phenomenon.

The influence of the white heat of the electrodes is seen still more distinctly in later researches of Hittorf[§] and Goldstein[||], which were made with very small pressure of gas. The older

[*] Proc. Roy. Soc. xxx. p. 155 (1880); xxxiii. p. 406 (1882).
[†] *Comptes Rendus*, lxxxiv. p. 346 (1877).
[‡] Wied. *Ann.* xxiv. p. 81 (1885).   [§] *Ibid.* xxi. p. 133 (1884).
[||] *Ibid.* xxi. p. 111 (1884).

observations do not show the decrease in resistance so strikingly, no doubt because, whilst the resistance at the kathode is greatly diminished by the formation of metallic vapour, the resistance of the positive light is increased by the higher pressure of gas.

But if by suitable means we heat the kathode in exhausted gas to the point of volatilization, we may obtain powerful currents even with small electromotive forces. In fact, Hittorf and Goldstein have observed these phenomena ; I will only mention of their results, that with a distance between the electrodes of 6 centim., one small element produced a constant current with high exhaustion and heating of the kathode to white heat.

§ 11. Warren DeLaRue and Müller*, in a comprehensive re-search, have endeavoured to show that glow-discharge and arc-discharge pass into each other in consequence only of change in the density of the gas. I wish here to express again my doubt (referring also to the criticism of Goldstein †) whether the authors did in fact have arc-light ; their assumption is also in direct contradiction with the previously published observation of Gassiot, on the passage of glow-discharge into arc-discharge at unaltered pressure.

Moreover, in accordance with the preceding consideration, the pressure is of small importance ; but everything depends upon whether the space between the electrodes is filled with incandescent metallic vapours or with ordinary gas. I have further had opportunity in my experiments to observe the passage of an arc-discharge into a glow-discharge, which is easily explained on the same principle.

If with the apparatus figured in fig. 2, at a pressure of 10 millim. the arc was lengthened until the resistance increased to the point of extinction, there appeared immediately in front of the anode a stratum of blue glow-light about 1 millim. thick and 10 millim. long, which, after a few seconds, disappeared with the light between the carbons.

If, then, the resistance became too great for the arc-discharge to continue, the conductivity of the still glowing metallic vapours was still sufficient for a short time to permit a much feebler current in the form of glow-discharge.

§ 12. In this concluding section, I should like to make some remarks on the luminosity of gases and vapours, which connect themselves with the experiments, already several times mentioned, of Hittorf. If, in electric glow-discharges, the electrodes came to an intense white-heat, the blue glow-

---

* Phil. Trans. clxxi. p. 65 (1879).
† Goldstein, *Fortschr. der Physik*, 1880.

light disappeared each time.   It follows from this, as well as from former observations of Hittorf* and W. Siemens † on the luminosity of flames, that up to the temperature of melting iridium, gases possess no perceptible emissive power, if they are not concerned in chemical changes or in electric discharges.   The cessation of luminosity at the white heat of the electrodes may perhaps be explained by the hot metallic vapours taking over the conduction, so that only a small fraction of the current goes through the hydrogen or nitrogen, which is not sufficient to bring it to luminosity. The conditions under which metallic vapours emit light may be quite different from those which hold good for ordinary gases.   The investigations of Schuster ‡ have shown, at least, that mercury vapour in a vacuum tube, from which every trace of other gas has been expelled, presents essentially different and, in fact, simpler phenomena, so that the electric discharge takes place without glow-light, dark space, or stratifications. Whether Schuster's explanation is correct, that the reason is to be found in the simpler constitution of mercury vapour, or whether metallic vapours generally do not show this simpler mode of discharge, seems to be worthy of further investigation. Since I have myself always seen an unstratified coherent mass of light filling the space between the electrodes in an arc of 3 centim. in length, the second possibility appears to me the more probable.

Physical Institute,
University of Strassburg.

XXXV. *Electromagnets.*—IV. *Cast Iron, Charcoal Iron, and Malleable Cast Iron.*   By R. H. M. BOSANQUET, *St. John's College, Oxford.*

To the Editors of the Philosophical Magazine and Journal.
GENTLEMEN,

THE following measures of permeabilities have been made on a number of rings of cast iron, charcoal iron, and malleable cast iron.   The magnetizing forces used varied in all cases from small forces to forces large enough to raise the metal to a condition but little removed from saturation.   I do not include at present any comparisons with formulæ, as the facts are perhaps best kept separate in the first instance. These measures complete all the experiments on rings which I have contemplated so far.

It may be convenient to summarize shortly some chief points of the results of all the experiments on rings.

* Wied. *Ann.* vii. p. 587 (1879).   † *Ibid.* xviii. p. 311 (1883).
‡ Proc. Roy. Soc. xxxvii. p. 317 (1884).

Permeabilities or Susceptibilities.

	Small inductions.	Maximum permeability.	Permeability for $\mathfrak{B}=10,000$.	For $\mathfrak{B}=14,000$*.
Cast iron	{ 50 80	170 250	30 80	
Malleable cast iron ...	{ 160 240	700 800	400 500	20 100
Wrought iron	{ 200 450	1800 2500	1200 2000	500 1000
Charcoal iron	{ 450 470	2900 } 3000 }	2000	600 860
Cast tool steel (hard)..	{ 40 50	145 155	100 130	70 86
„ „ (soft) ...	{ 90 120	420 460	350 } 450 }	200

Saturation-points.
$\mathfrak{B}=$

Cast iron	9,000—14,000.
Malleable cast iron	14,000—16,000.
Wrought iron } Charcoal iron }	17,000—19,000.
Cast tool steel, both hard and soft	20,000.

The malleable cast-iron rings were supplied to me by Messrs. Crowley, of Sheffield. The material cuts exactly like charcoal iron; and it seemed probable that its magnetic qualities might be similar to those of charcoal iron. In this case the possibility of casting the material would have been of the highest importance with reference to dynamo machines.

The results for ordinary cast iron show that it is wholly unfit for use in dynamo machines; the low saturation-point being particularly objectionable. The malleable cast iron would undoubtedly be a great improvement on ordinary cast iron; but still inferior to wrought iron.

It may be noted that the variations of temper in the different rings of malleable cast iron did not appear to correspond to any recognizable differences, either mechanical or magnetic.

About the time these experiments were drawing to a close I became aware, by a notice in 'Nature,' that Dr. Hopkinson had communicated to the Royal Society a series of investigations apparently similar to my own. I have not yet been able to learn any thing about the contents of the paper in question; but considering the diversity of the properties of different specimens, as well as of the methods in use, I still hope that my results may not be without usefulness.

* As before, $\mathfrak{B}$ stands for the magnetic induction, or number of lines of force across unit area; μ for permeability or susceptibility.

TABLES OF RESULTS.

Cast-Iron Ring, Q (*Medium Hard*).

Mean diameter .... = 21·925 centim.
Bar-thickness .... = 1·450 „
Number of coils .... = 7086.

B.	μ obs.	B.	μ obs.
78	75	5680	159
624	124	6199	144
802	100	6877	136
2357	210	7415	104
3013	214	8621	92
3114	205	8862	78
3683	192	9793	75
4122	201	10633	64
4253	191	10756	46
4481	188	12161	46
4952	179		

Cast-iron Ring, N (*Medium Hard*).

Mean diameter .... = 10·1 centim.
Bar-thickness .... = 1·321 „
Number of coils .... = 1138.

B.	μ obs.	B.	μ obs.
24	61	3032	219
159	75	3605	256
412	94	4089	212
703	121	4894	199
1226	154	5243	188
1240	155	6580	146
1316	159	7772	111
1752	189	8283	93
2471	215	9497	71
2558	211	10786	35
2616	204		

Cast-Iron Ring, T. Cylinder Iron (*Hard*).

Mean diameter .... = 21·625 centim.
Bar-thickness .... = 1·936 „
Number of coils .... = 7223.

B.	μ obs.	B.	μ obs.
67	55	4146	142
267	75	4601	127
2007	169	4888	117
2424	167	5327	104
2886	163	5693	93
3239	163	6459	75
3253	160	7177	60
3397	154	7639	52
3668	151	8181	44
3955	143	9098	33

Cast-Iron Ring, P (*Medium Hard*).

Mean diameter .... = 10·0 centim.
Bar-thickness .... = 1·3095 „
Number of coils .... = 2504.

B.	μ obs.	B.	μ obs.
37	52	3921	200
229	81	4705	201
581	109	5543	193
908	127	6163	171
1514	158	7258	137
1630	159	8607	107
2033	175	9665	87
2614	206	11123	62
2522	199	13038	29
3264	190		

Swedish Charcoal-Iron Ring, S (Soft).

Mean diameter .... = 11·4 centim.
Bar-thickness .... = 1·547 „
Number of coils .... = 560.

B.	μ obs.	B.	μ obs.
87	453	10379	2139
1345	1776	10514	2013
3397	2750	11148	1903
5149	3027	12480	1322
6201	2954	12980	1072
7616	2793	13587	821
8034	2675	14059	606
8182	2620	14463	471
8411	2552	15366	276
9907	2291	17146	90

Malleable Cast-Iron Ring, Z (Hard).

Mean diameter......... = 10·0 centim.
Bar-thickness .... = 1·332 „
Number of coils ...... = 1224.

B.	μ obs.	B.	μ obs.
84	237	7748	706
839	422	7829	679
3529	767	8011	666
3894	753	8600	650
4543	768	9167	567
4726	775	9573	515
5273	828	9938	427
5760	796	10445	378
6003	784	11034	267
6592	756	11926	175
6693	749	13183	95
7200	723	14765	40
7504	717		

Cast-Iron Ring, C (Soft).

Mean diameter ...... = 10·2 centim.
Bar-thickness......... = 1·0325 „
Number of coils .... = 2098.

B.	μ obs.	B.	μ obs.
40	77	3891	226
236	86	4447	214
578	115	5454	216
865	133	6184	197
1346	164	7226	158
1624	176	8442	120
2286	199	9241	101
2814	219	10769	73
3509	230	13983	38
3570	250		

Swedish Charcoal-Iron Ring, R (Soft).

Mean diameter .... = 10·5 centim.
Bar-thickness .... = 1·304 „
Number of coils .... = 517.

B.	μ obs.	B.	μ obs.
79	467	10666	2059
1527	1916	11281	1870
4372	2866	11723	1743
5189	2895	12569	1426
6803	2799	13203	1223
8149	2633	14087	858
8418	2588	14894	585
8763	2540	15336	433
8841	2477	18277	107
9455	2344		

Malleable Cast-Iron Ring, U (*Medium Hard*).

Mean diameter .... = 10·0 centim.
Bar-thickness .... = 1·335 "
Number of coils......... { = 503. / = 1981.

B.	μ obs.	B.	μ obs.
33	22	4575	737
200	231	5228	781
741	388	7095	812
747	337	8085	574
829	315	9523	560
1175	377	10569	418
1531	430	11110	330
2252	539	11857	212
1942	497	13631	78
2988	611	13995	18
3548	652		

Malleable Cast-Iron Ring, V (*Soft*).

Mean diameter .... = 10·01 centim.
Bar-thickness .... = 1·341 "
Number of coils......... = 1162.

B.	μ obs.	B.	μ obs.
70	173	8913	525
495	238	9091	502
1414	387	9268	499
2891	547	9584	481
3254	578	10057	448
4023	612	10393	407
4634	631	10590	385
5719	665	10669	386
5995	649	11773	270
7060	541	12621	195
7888	571	13015	152
8125	558	13568	109
8480	549	15658	46
8716	520		

Malleable Cast-Iron Ring, W (*Hard*).

Mean diameter .... = 10·05 centim.
Bar-thickness .... = 1·336 "
Number of coils......... = 1189.

B.	μ obs.	B.	μ obs.
84	199	8352	653
708	329	8805	603
2211	583	9296	525
3518	726	9925	446
4363	776	10220	392
4520	760	11320	273
5542	796	11792	196
5896	789	12185	146
6348	774	13129	97
7134	761	15035	40
8097	688		

Malleable Cast-Iron Ring, Y (*Medium Hard*).

Mean diameter .... = 10·075 centim.
Bar-thickness .... = 1·131 "
Number of coils......... = 1207.

B.	μ obs.	B.	μ obs.
75	163	7585	752
478	281	7741	739
1673	518	7702	753
3413	719	8363	718
4435	774	8947	633
4707	776	9433	577
5057	794	10114	465
5251	784	10406	420
5874	791	11048	291
6546	777	11437	191
6866	793	12409	120
6866	782	12915	100
7294	762	15016	41

Malleable Cast-Iron Ring, X (*Soft*).

Mean diameter .... = 10·115 centim.
Bar-thickness .... = 1·304 „
Number of coils .... = 1220.

𝕭.	μ obs.	𝕭.	μ obs.
62	178	7144	735
276	146	7628	724
1293	491	7669	755
3784	712	8759	715
3976	701	9142	626
4395	717	9526	618
4622	767	10373	495
5045	746	11080	417
5247	746	11907	276
5449	753	12412	217
5853	754	12876	173
6196	759	13562	115
6781	762	15762	47

XXXVI. *On the Influence of Heat on the Rate of Chemical Change.* By JOHN J. HOOD, *D.Sc.* (*Lond.*)*.

THE accelerating action of heat on the rate at which a chemical change progresses has been made the subject of investigation by several chemists. The amount of work that has been done towards the elucidation of this side of the great problem of chemical action, expressing the rate as a function of the temperature, is as yet too insignificant to allow of any deductions being drawn relative to the probable mechanical processes that take place in a medium containing a chemical system undergoing change. · Considered in the light of molecular interdiffusion, it would seem probable that the relation between the rate of change of different chemical systems comprising two or more active bodies (active in a chemical sense) and the temperature should be of the same type; and the experiments that have been made on this subject all seem to show this in common, that the rate of the change increases very rapidly for small increments of temperature.

Warder†, in his experiments on the speed of saponification of ethylic acetate, was led to infer that the increase of speed in this reaction is approximately as the second power of the temperature.

Mills and Mackey‡, studying the evolution of hydrogen from zinc and hydric sulphate at different temperatures, a case of a chemical system of a non-homogeneous character,

* Communicated by the Author.
† American Chemical Journal, vol. iii.   ‡ Phil. Mag. [5] xvi.

found a relation between what they call the " zero strength "
and the temperature, represented by the equation

$$s = a + \frac{b + ct}{d + t}.$$

Urech [*], from experiments on the speed of inversion of cane-
sugar by acids at different temperatures, expresses the rate as
a function of the temperature of the form $\alpha t + \alpha' t^2 + \alpha'' t^3$.

More recently Menschutkin [†] has studied this subject, em-
ploying the rates of formation of ethylic acetate, acetanilide,
and acetamide. His results show that if ϵ and ϵ' represent
the amounts of these bodies that are formed during the interval
of one hour at temperatures $\theta°$ and $\theta° + n°$, the value of $\epsilon' - \epsilon$
passes through a maximum at a definite temperature.

Lemoine[‡], with reference to the simplest case of a chemical
change represented by the equation

$$\frac{dy}{dt} = A(p - y),$$

such, for instance, as the action of hydric peroxide on a soluble
iodide in presence of sodic thiosulphate, as worked out by
Harcourt and Esson, says:—" Un fait très général et très
digne de remarque est l'extrême accroissement du coefficient
A, c'est-à-dire de la vitesse de décomposition avec la tempé-
rature. Si θ est la température, A paraît varier avec elle
suivant une formule exponentielle $A = a'a^\theta$. Ce fait, résultat
d'une multitude d'expériences, paraît corrélatif de la nature
même de ce mouvement intérieur qui constitue la température
d'un corps."

The " multitude d'expériences," however, would seem to
imply the common observation of the great increase in rapidity
of a chemical reaction with small increase of temperature.

In a paper published in this Journal[§], in which the oxida-
tion of ferrous sulphate by potassic chlorate was the subject
of investigation, it was shown that the course of the oxidation
was represented by the equation

$$\frac{dy}{dt} = -\mu f(\theta) y^2. \quad \cdots \quad \cdots \quad (1)$$

Integrating and writing it in the form $y(a + t) = b$, it is clear
that for two experiments made at different temperatures $\theta°$
and $\theta° + n°$, the relation $\dfrac{b}{b'} = \dfrac{f(\theta + n)}{f(\theta)}$ holds.

[*] *Berichte d. d. Chem. Gesell.* xvi. p. 762.
[†] *Journ. Prakt. Ch.* 1884.
[‡] " Études sur les Équilibres chimiques," p. 178 (Fremy's *Ency. Chim.*).
[§] Phil. Mag. [5] vi.

It was stated that the few experiments that were made to determine the form of this temperature function seemed to indicate that $f(\theta) = \theta^2$, or that the rate of change varies as the square of the temperature.

This reaction has again been made the subject of investigation, with regard to temperature, and the results obtained are comprised in the following tables.

The mode of performing the experiments has already been fully given in several papers in this Journal, so that it will be sufficient merely to give the strengths of the solutions employed in the work. Each experimental solution consisted of ·5637 gram iron (Fe'') as sulphate, ·2057 gram $KClO_3$, and 3·099 grams free hydric sulphate, made up to a volume of 260 cubic centims. contained in a glass flask and maintained at the required temperature in a large water-bath. The course of the oxidation was observed by withdrawing 10 cubic centims. of the solution, and titrating with permanganate at indefinite intervals of time, to determine the equation $y(a+t) = b$; y being cubic centim. permanganate and t time in minutes. Two, and in many cases four, experimental solutions were employed at each temperature, and the values for a and b that are given are the means of these. Every precaution was taken to keep the temperature of the measuring pipettes, permanganate, &c. the same as that of the experimental solution,—the thermometers employed being very fine ones, by Negretti and Zambra, divided to tenths, on which ·02° could be read easily; and in every case where an experiment fluctuated by so much as $\pm$ ·1° C., the results were rejected.

Although the experiments tabulated below are only comprised between the narrow limits of 10° and 32° C., it was found that outside these extremes the results were liable to be vitiated by several sources of error. Below 10° C. the progress of the oxidation was so slow that during the long period that the experiments had to be continued there was liability of atmospheric oxidation taking place; besides, a small error in the permanganate titration made a comparatively large one in the time, whereas above 32° C. the speed was much too rapid to obtain accurate measurements. Between these narrow limits of temperature the rate of oxidation increases over sevenfold.

In the figure, the course of a few of the experiments are plotted from the experimental numbers, and these curves show at a glance the great differences in the rates of oxidation at the various temperatures.

Curves showing the course of the Oxidation of Ferrous Sulphate by
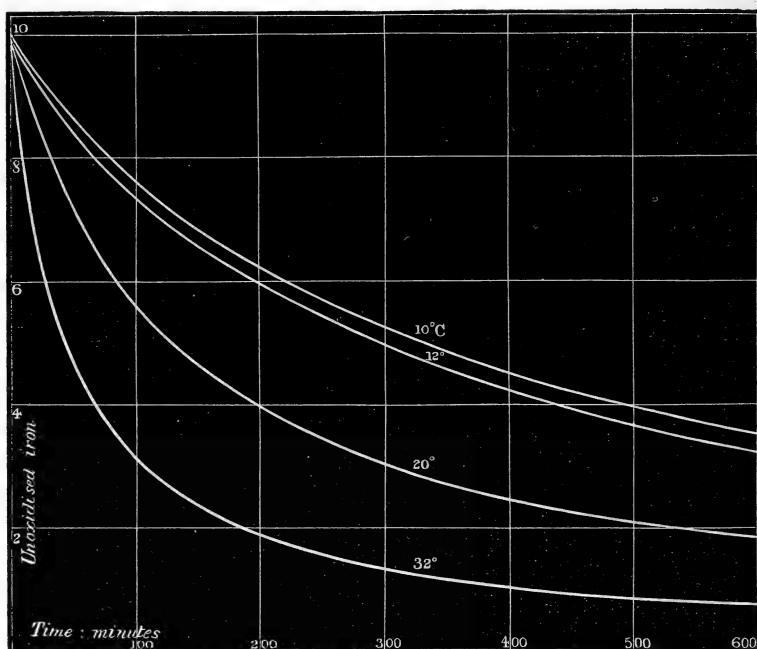Potassic Chlorate at different Temperatures.

TABLE I.

Temp. C°.	$a.$	$b.$	Ratio $\dfrac{b_n}{b_{n+1}}$.
10	330·8	3327·8	......
11	301·6	3025	1·100
12	274·7	2752·9	1·098
13	250	2503	1·099
14	227·5	2282·7	1·096
15	206·6	2055·7	1·110
16	194·3	1920·8	1·070
17	174·2	1733	1·109
18	159	1577·4	1·098
19	147·1	1452·6	1·086
20	134·4	1325·4	1·096
21	124	1216·8	1·089
22	114·9	1123	1·083
23	102·6	1002·3	1·120
24	94·8	924·5	1·084
25	89·9	869	1·064
28	68·5	654·8	1·099
30	58·7	551·2	1·090
32	50·3	465·3	1·088
		Mean	1·093

From the foregoing table it will be seen that the ratio $\dfrac{b_n}{b_{n+1}}$ has, as nearly as possible, a constant value, the mean from all the experiments being equal to 1·093. It would seem therefore that $f(\theta)$ may be written in an exponential form and equation (1) becomes

$$\frac{dy}{dt} = -a\alpha^\theta y^2.$$

In this particular reaction, taking the mean value for α as given above, and the rate of oxidation at 10° C. as unity, the rate ρ at temperature $\theta°$ C. is represented by the equation

$$\rho = (1\cdot093)^{\theta-10°}.$$

In the following Table the rates at the different temperatures, as determined experimentally by the ratio $\dfrac{b_{10}}{b_\theta}$, and as calculated from the above equation, are given ; and it will be seen that there is a close agreement between the two series of numbers.

TABLE II.

Temp. C°.	Rate of oxidation.	Calculated rate of oxidation.	Temp. C°.	Rate of oxidation.	Calculated rate of oxidation.
10	1·00	......	20	2·51	2·43
11	1·10	1·09	21	2·73	2·66
12	1·21	1·19	22	2·96	2·91
13	1·33	1·31	23	3·32	3·18
14	1·46	1·43	24	3·59	3·47
15	1·62	1·56	25	3·83	3·80
16	1·73	1·70	28	5·08	4·96
17	1·92	1·86	30	6·04	5·92
18	2·11	2·04	32	7·15	7·07
19	2·29	2·23			

In a previous paper, already referred to, it was suspected that $\rho \propto \theta^2$; but as the experiments were too few in number and between too narrow limits of temperature, the actual results were not given. It may be of interest, therefore, to see how far the present series of experiments bear this supposition out.

Representing the relation between rate and temperature by the equation $\rho = \kappa(\theta + n)^2$, taking $\rho_{10} = \kappa(10 + n)^2 = 1$, the following are the values obtained for n :—

<div align="center">TABLE III.</div>

Rate of oxidation, ρ.	Value for n.	Rate of oxidation, ρ.	Value for n.	Rate of oxidation, ρ.	Value for n.
1·10	10·5	1·92	8·1	3·32	5·8
1·21	10	2·11	7·7	3·59	5·6
1·33	9·6	2·29	7·5	3·83	5·6
1·46	9·2	2·51	7·1	5·08	4·3
1·62	8·3	2·73	6·8	6·04	3·7
1·73	9	2·96	6·6	7·15	3·1

From this Table it will be seen that n, instead of having a constant value, gradually diminishes as the temperature increases, but that for a few consecutive experiments the differences are such as might be referred to experimental errors, and so lead to the erroneous supposition that $\rho \propto \theta^2$.

So far as these experiments go, it would seem probable that, for this reaction at least, the temperature function is of an exponential form. Indeed, in many cases of chemical change it is a common observation that the speed increases very rapidly with the temperature, being, as Lemoine remarks, characteristic of an exponential form. In the course of some experiments on retardation, in which ferrous chloride was the material employed, instead of sulphate as in the present case, it has been found that here also, in presence of agents that retard the oxidation very considerably, the relation between rate and temperature may be represented in the form $\rho = a\alpha^\theta$. A full account of these experiments, however, will, it is hoped, be given at a future time.

XXXVII. *On the Generation of Electric Currents by Sulphur Cells.* By SHELFORD BIDWELL, *M.A., LL.B.*[*]

IN a communication recently made to the Physical Society[†] I ventured the suggestion that the electric conduction of selenium, when prepared in such a form as to be sensitive to light, was, in the literal sense of the term, electrolytic. Selenium itself indeed could hardly be supposed to be an electrolyte; but it was pointed out that when selenium was "annealed" in contact with metallic electrodes, metallic selenides would, at least in most cases, be formed in sufficient quantity to account for the electrolytic phenomena observed; and that even if this were not the case when the electrodes consisted of such a metal as platinum, yet the necessary metallic element

[*] Communicated by the Physical Society: read June 27, 1885.
[†] Phil. Mag. August 1885.

might possibly be found in the lead, iron, and arsenic which are contained as impurities in ordinary commercial selenium. Little direct evidence was offered in support of this view; but it was shown that sulphur, when mixed with a certain proportion of sulphide of silver and arranged in the form of a " cell " with silver electrodes, exhibited many of the properties of crystalline selenium, especially that of having its electrical resistance temporarily diminished under the influence of light. Analogy therefore tended to confirm the opinion which I had been led to entertain.

While observing the secondary or polarization-currents which are generated by sulphur cells (as by those made with selenium), after being disconnected from a battery, certain effects were noticed which seemed to indicate that when the electrodes consisted of two different metals, a sulphur cell might be capable of originating and maintaining an independent or primary current. Experiments were therefore made with the object of investigating this point; and the present paper contains an account of the results obtained. I have hardly attempted to connect them together by any complete theory: of some of them, indeed, I can offer no explanation whatever; others appear to be in direct opposition to what might have been expected. But, so far as I have been able to ascertain, they are entirely novel, and of sufficient interest to be worthy of record.

(1) A slip of mica was wound with two parallel wires of silver and copper 1 millim. apart, and melted sulphur containing a small quantity of precipitated sulphides of silver and copper was spread over one surface. It is not known what proportion of the sulphides was contained in the mixture, because the bulk of them sank to the bottom of the crucible in which the sulphur was melted. When cold, the cell was connected with a reflecting galvanometer, and was found to generate a small but steady current, indicated by a deflection of about 20 scale-divisions. When the connections of the cell were reversed, the current was reversed. It was therefore not due to any thermo-effect in the circuit. The direction of the current was from silver to copper through sulphur: its strength was *diminished* by exposure to light, and *increased* by rise of temperature. Connecting the free ends of the silver and copper wires and heating the junction, it was found that the thermo-current thus produced passed (as usual) from copper to silver through the junction. The increase of current by heat was therefore not to be accounted for by thermo-electric action, for that would produce the opposite effect.

The action is almost certainly of the same nature as that which occurs in an ordinary voltaic cell.

(2) It appeared desirable to construct a cell which, though unsuitable for experiments with light, would have a much smaller resistance than one of the form last described. A plate of copper 3 centim. square was heated, and upon it was spread a mixture consisting of 5 parts of sulphur and 1 part of sulphide of copper. A plate of silver previously heated was then laid on the melted mixture and the two plates squeezed together, thus forming a sandwich-like cell. The thickness of the copper plate was 2·75 millim., of the silver plate ·60 millim., and of the completed cell 3·65 millim.; the thickness of the layer of sulphur was therefore ·3 millim. When this cell (after cooling) was connected with the galvanometer, the spot of light was violently deflected off the scale. Dr. Fleming was kind enough to make a very accurate measurement of its electromotive force by comparison with one of his standard Daniell cells. It was found to be ·0712 volt, and its internal resistance was 6537 ohms. As in the case of the former cell, the direction of the current is from silver to copper; and there can be no doubt that it is of a voltaic nature. At the time of writing, the cell has been in existence nearly seven weeks, and it is now, I believe, quite as powerful as at first.

(3) It was thought that the internal resistance might be further reduced by adding a larger proportion of sulphide to the sulphur. Another cell was therefore constructed similar in all respects to that last described, except that the sulphur and copper sulphide were mixed in equal proportions. Its internal resistance was enormously lower, being only 13 ohms, but its E.M.F. was also lower, being ·0071 volt.

(4) A layer of precipitated sulphide of copper was placed between plates of copper and silver which were squeezed together in a screw-press. The resistance of this arrangement was a small fraction of an ohm; but when connected with the galvanometer, it gave no indication whatever of a current. It seems, therefore, that a certain amount of free sulphur is necessary for the generation of an electromotive force by cells containing copper sulphide.

(5) Two parts of copper sulphide were mixed with one of sublimed sulphur, and the powder was compressed between plates of copper and silver. This cell gave a very small current, indicated by a galvanometer-deflection of 2 or 3 scale-divisions. The deflection was reversed as often as the connections with the binding-screws of the cell were reversed; and the existence of a real, though very small, electromotive force was undoubted. The internal resistance was ·088 ohm.

(6) The last-mentioned cell was taken to pieces and remade after the addition of about an equal part of sublimed sulphur to the mixture of sulphur and sulphide. Its resistance was now found to be many megohms, yet it produced a larger galvanometer-deflection than before.

(7.) Once more the cell was taken to pieces and a little more sulphide added. When remade, its resistance was at first about 2700 ohms; but it varied considerably. It produced a galvanometer-deflection of about 100 divisions, which in a few minutes increased in a somewhat irregular manner to 250 divisions. It was then disconnected from the galvanometer, and, when again connected after an interval of six hours, it deflected the spot of light off the scale. Shunting the galvanometer (the resistance of which was 3483 ohms) with a coil of 300 ohms, the deflection amounted to 130 divisions; and on the following day with the same shunt, the deflection was at first about 250 divisions, rapidly diminishing, however, when the circuit was closed.

(8) A cell was made by compressing precipitated silver sulphide unmixed with any free sulphur between plates of silver and copper. When connected with the galvanometer, this cell produced a deflection which, with a shunt of 35 ohms, exceeded 400 divisions. But in this case the *silver* was the negative plate, the direction of the current being from copper through sulphide to silver. The E.M.F. was less than that of the cell described in (2).

(9) Another cell was made in the same manner as that described in (2); but the sulphur was mixed with sulphide of silver instead of sulphide of copper. This gave a strong current in the same direction as that produced when sulphide of copper was used, and opposite to that generated by the cell containing silver sulphide without free sulphur.

(10) Pure sulphur was melted on a clean plate of copper, and, when just liquid, a warmed plate of silver was laid upon it and pressed down with a weight until cold. This cell gave a strong current from silver through sulphur to copper. Sulphides were of course formed during the process of construction.

(11) A melted mixture of sulphur and silver sulphide was spread upon a copper plate, and a plate of silver pressed upon it. When cold, the silver plate was split off with a knife, and a piece of silver-leaf, sufficiently thin to appear blue by transmitted light, was attached (by rubbing) to the exposed surface of the mixture. As before, there was a comparatively strong current from the silver to the copper. The silvered surface was then exposed to the light of burning magnesium wire, and

the immediate movement of the spot of light through 50 scale-divisions indicated a *diminution* of the current. When the magnesium was extinguished, the current at once increased to its original strength. When a nearly red-hot brass rod was held at a distance of 3 centims. from the silvered surface, the current slowly *increased* in strength; and when the hot rod was removed, the current was again slowly diminished. The effects both of light and of heat were verified by many repetitions of the experiments. These results which, so far as regards the effect of light, were unexpected, are of the same character as those described in (1). I have elsewhere* given strong reasons for believing that the combination of sulphur with silver is assisted by the influence of light. If this is so, it is certainly a remarkable fact that increased corrosion of the silver electrode should be accompanied by diminution of the current.

Two days afterwards the silver-leaf had become much discoloured, and was in some parts quite black. When connected with the galvanometer the cell gave a current of nearly the same strength as before; but now it was found to be slightly increased by light as well as by heat; and it is probable that the light as such exerted no influence whatever, the observed effect being really due to the incidental rise of temperature.

(12) The silver-leaf was scraped off, and the surface of the sulphur mixture having been cleaned from all visible traces of free silver with fine emery-cloth, a piece of thin gold-leaf was pressed upon it. It was found very difficult to make it adhere satisfactorily. The cell, when connected with the galvanometer, gave no indication whatever of a current. When the cell described in (2) was also inserted in the circuit, the spot of light was deflected, showing that the first cell was quite able to conduct electricity, and that its failure to originate a current was not owing to bad contact between the gold-leaf and the sulphur mixture.

(13) A cell containing a mixture of sulphur and silver sulphide between plates of silver and iron was found to have an E.M.F. of ·023 volt, or about one third of that of the silver-copper cell described in (2). The direction of the current was the same.

(14) A cell was made by melting sublimed sulphur upon a plate of copper and pressing a plate of iron upon the melted sulphur. On connecting it (when cold) with the galvanometer, there was no indication of any current. Nevertheless the cell was found to conduct electricity very well when a

* Phil. Mag. August 1885.

battery was also placed in the circuit. Sulphide of copper was of course formed by the action of the hot sulphur upon the copper.

(15) A melted mixture of 5 parts of sulphur with 1 part of copper sulphide was pressed between plates of silver and iron, and cooled. When first made, this cell generated a sufficiently strong current to deflect the galvanometer-needle as far as the stop would allow; but two hours later, when an attempt was made to measure the E.M.F., it was found to have almost completely disappeared, being less than a hundredth of that of the cell described in (2). The E.M.F. was temporarily restored by connecting the iron and silver plates with the positive and negative terminals of a battery of ten Leclanché cells for a few minutes. The result was of course merely a polarization-current.

(16) Two silver wires A, B were imbedded in a fused mass consisting of equal parts of sulphur and copper sulphide. When cold, the wire A was connected with the carbon pole of a battery of ten Leclanché cells, and the wire B with the zinc pole. After the current had passed for about a second, the cell was detached from the battery and connected with the galvanometer. A current was at once indicated in the direction A B, *i. e.* in the *same* direction as that of the battery-current which had been caused to pass through the cell. This experiment was repeated many times and on different days, with the same result*. A period of some seconds necessarily elapsed between the separation of the cell from the battery and its attachment to the galvanometer. In order to render this interval as short as possible, the apparatus was so arranged that by depressing a key the transfer could be effected in a small fraction of a second. It was then found that the first effect of the transfer was a strong *momentary* current in the direction B A, which was immediately followed by the more permanent current previously observed in the direction A B. With the view of retarding the first effect, a battery of two Leclanché cells was used, and the connection was made for a longer period. After the battery had been connected for one minute, the cell was transferred to the galvanometer by means of the key, and the swing of the spot of light through 280 scale-divisions again indicated a current in the direction B A. Though this was not, as before, a current of only momentary duration, it rapidly decreased in strength, becoming zero in almost exactly 30 seconds. After zero was passed, a current was at once set up in the opposite direction A B, which

* The experiments described in the remainder of this paragraph were made after the paper was read.

in 30 seconds produced a deflection of 70 divisions, increasing
to a maximum of 131 divisions in 10 minutes.   The current
then slowly diminished; and in 5¾ hours after the commence-
ment of the experiment the deflection had fallen to 17 scale-
divisions.   At this point the observations were discontinued.
In the accompanying curve the abscissæ represent the time
in hours, and the ordinates the current in scale-divisions.   The
current of 30 seconds' duration in the direction B A is not
represented.
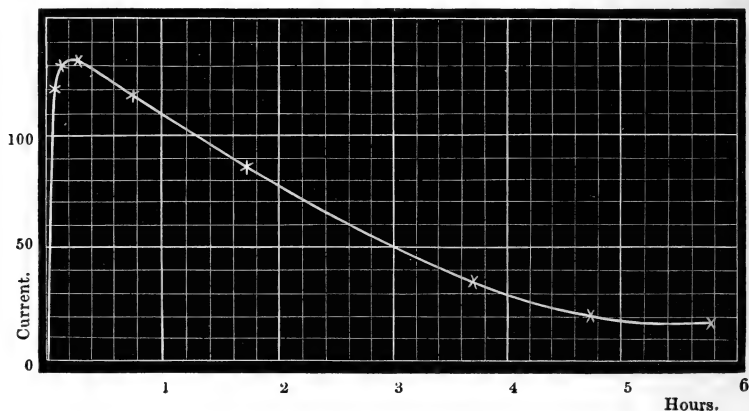
On another occasion, when the two Leclanché cells had
been connected for 3 minutes, the secondary current from B
to A decreased still more slowly than in the last-mentioned
experiment, vanishing in 3½ minutes.   The current which
followed in the direction A B attained its maximum, indicated
by 155 divisions, in 6½ minutes, and then steadily decreased
for nearly 4 hours, when it again became zero.   The spot of
light did not, however, remain stationary, but moved steadily
on, indicating a second reversal of the current.   In one hour
after zero had thus been crossed for the second time, the gal-
vanometer-deflection was 12 scale-divisions; and 4½ hours
later, when the last observation was made, it had increased to
20 divisions.   In both these experiments the galvanometer
(of which the resistance was nearly 3500 ohms) was shunted
with a coil of 100 ohms.

These alternating currents are probably of the same nature
as those which Faraday found to be generated when copper and
silver, or two pieces of copper, or two pieces of silver, were
immersed in a solution of potassium sulphide*.   The wires
are alternately protected from the action of the free sulphur
by an investing coat of sulphide.

* Exp. Res. §§ 1911 and 2036.

Summary.

Plates of silver and copper imbedded in a mixture of sulphur with sulphides of copper or silver constitute a cell which at the ordinary temperature is capable of generating and maintaining a constant current, the silver being the positive element. Such a cell, in which the mixture consisted of 5 parts of sulphur with one of copper sulphide between plates 3 centim. square and ·3 millim. apart, had an E.M.F. of ·0712 volt and an internal resistance of 6537 ohms.

If the proportion of copper sulphide to sulphur is increased, the internal resistance of the cell is diminished; but its E.M.F. is also diminished.

A cell containing copper sulphide unmixed with free sulphur fails to produce any appreciable current.

A cell containing silver sulphide only generates a current in the opposite direction to that produced when the sulphide is mixed with free sulphur.

Copper used in conjunction with iron or gold gives no current whatever at the ordinary temperature.

The current generated by a silver-copper cell containing free sulphur mixed with sulphide is diminished by the action of light and increased by heat. It has not been ascertained whether the effect is upon the E.M.F. or the internal resistance, or both.

If a battery-current is caused to pass for a short time through a cell consisting of two silver electrodes imbedded in a mixture of sulphur and copper sulphide, the cell, after being disconnected from the battery, will generate a current of very short duration in the direction opposite to that of the battery-current, followed by a current which may be maintained for several hours in the *same* direction as the battery-current. A second reversal has in one case been found to occur after an interval of four hours.

The experiments, of which an account is here given, must be considered as being merely of a preliminary nature. A complete investigation of the phenomena in question would require more time than I am at present able to devote to the subject.

Addition, August 3rd.

From (4), (5), and (6) it appears that a cell consisting of copper and silver plates is incapable of generating a current unless a certain proportion of free sulphur is mixed with the sulphide. Thinking that the function of the free sulphur

might be merely to form silver sulphide by direct combination with the silver, I constructed a cell as follows :—A layer of copper sulphide was spread upon a plate of copper ; a polished steel plate was laid upon the sulphide, and the whole was strongly compressed in a vice. The steel plate was then removed, and a thin layer of silver sulphide was spread upon the smooth surface of the copper sulphide. The cell was completed by pressing a silver plate upon the silver sulphide. This was found upon trial to give a current which, with an external circuit of low resistance, was many times stronger than that generated by any of the cells previously made. It seems to be exactly analogous in its action to a Daniell cell consisting of plates of zinc and copper in solutions of zinc sulphate and copper sulphate. The quantity of the copper sulphide would be gradually diminished, copper being deposited on the copper plate, while the quantity of silver sulphide would continually increase with consumption of the silver.

In conclusion, it seems probable that, by selecting such metals as experiment might prove to be better suited for the purpose than silver and copper, a cell might be constructed upon the principle of that described in the above paragraph which would be of practical and commercial value.

XXXVIII. *Notes on the Seat of the Electromotive Forces in a Voltaic Cell.* By J. HOPKINSON, *M.A., D.Sc., F.R.S.**

THE following is an expansion of some short remarks I made when Dr. Lodge's paper was read at the Society of Telegraph Engineers.

I. *The controversy between those who hold that the difference of potential between zinc and copper in contact is what is deduced by electrostatic methods, and those who hold that it is measured by the Peltier effect, is one of the relative simplicity of certain hypotheses and definitions used to represent admitted facts.*

Taking thermoelectric phenomena alone, we are not imperatively driven to the conclusion that the difference of potential between zinc and copper is the small quantity which the Peltier effect would indicate ; but by assuming with Sir W. Thomson that there is an electric property which may be expressed as an electric convection of heat, or that electricity has specific heat, we may make the potential difference as great as we please without contradiction of any dynamical principle or known physical fact. Let us start with the physical facts, and introduce hypothesis as it is wanted.

These are, as far as we want them :—(1) If a circuit consist of one metal only, the electromotive force around the circuit is nil however the temperature may vary in different parts ; this of course neglecting the thermoelectric effects of stress and magnetism discovered by Sir W. Thomson. (2) If the circuit consist of two metals with the junctions at different temperatures t_1, t_2, then the electromotive force round the circuit is the difference of a function of t_2 and of the same function of t_1. According to Prof. Tait the function is

$$b(t_2 - t_1)\left(\mathrm{T} - \frac{t_2 + t_1}{2}\right),$$ or, as we may write it, $\mathrm{A} + \mathrm{B}t_2 - \mathrm{C}\dfrac{t_2{}^2}{2} -$

$\left\{ \mathrm{A} + \mathrm{B}t_1 - \mathrm{C}\dfrac{t_1{}^2}{2} \right\}$; the series may perhaps extend further, but, according to Tait's experiments, the first three terms are all that are needed.

Now, but for the second law of thermodynamics we should naturally assume that $\mathrm{A} + \mathrm{B}t_2 - \dfrac{\mathrm{C}t_2{}^2}{2}$ was the difference of potentials at the junction of temperature t_2, and $\mathrm{A} + \mathrm{B}t_1 - \dfrac{\mathrm{C}t_1{}^2}{2}$ at the junctions of temperature t_1 ; we should further assume that what the unit of electricity did was to take energy $\mathrm{A} + \mathrm{B}t_2 - \dfrac{\mathrm{C}t_2{}^2}{2}$ out of the region immediately around the hot junction with disappearance of that amount of heat, and to take energy $\mathrm{A} + \mathrm{B}t_1 - \dfrac{\mathrm{C}t_1{}^2}{2}$ into the region immediately surrounding the cold junction, with liberation of that amount of heat. Now apply the second law of thermodynamics in the form $\Sigma \dfrac{q}{t} = 0$, and we have

$$\mathrm{A}\left(\frac{1}{t_2} - \frac{1}{t_1}\right) - \mathrm{C}\frac{t_2 - t_1}{2} = 0,$$

whence it follows that $\mathrm{A} = 0$, which may be, and that $\mathrm{C} = 0$, which is contrary to experiment. The current then must do something else than has been supposed, and the hypotheses differ in expression at least as to what that something else is. The fact to be expressed is simply this : when a current passes in an unequally heated metal, there is a reversible transference of heat from one part of the metal to another, whereby heat is withdrawn from or given to an element of the substance when a current passes through it between points differing in temperature, and is given to or withdrawn from that element if the current be reversed. Sir W.

Thomson proved that this follows from the fact of thermo-electric inversions and the second law of thermodynamics, and verified the inference by experiment, his reasoning being quite independent of any hypothesis.

Suppose wires of metals X and Y are joined at their extremities, and the junctions are kept at temperatures t_2, t_1. The observed electromotive force around the circuit is $f(t_2) - f(t_1)$ or within limits according to Tait, $B(t_2 - t_1) - \frac{1}{2}C(t_2{}^2 - t_1{}^2)$. The work done or dissipated by the current when unit of electricity has passed is $f(t_2) - f(t_1)$, and this is obtained by abstraction of heat from certain parts of the circuit and liberation of heat at other parts by a perfectly reversible process. Let $F(t_2)$ be the amount of heat which disappears from the region surrounding the junction t_2 when unit of electricity has passed from X to Y. Let an element of the wire X have its ends at temperatures t and $t + dt$, and let the quantity of heat abstracted from this element when unit of electricity passes from t to $t + dt$ be represented by $\phi(t)dt$, and let the same for Y be represented by $\psi(t)dt$. By the first law of thermodynamics we have

$$F(t_2) + \int_{t_2}^{t_1} \psi(t)dt - F(t_1) + \int_{t_1}^{t_2} \phi(t)dt = f(t_2) - f(t_1),$$

and by the second law, since the transference of heat from part to part is reversible,

$$F(t_2)/t_2 - F(t_1)/t_1 + \int_{t_1}^{t_2} \phi(t)/t \cdot dt - \int_{t_1}^{t_2} \psi(t)/t \cdot dt = 0.$$

Differentiating we have

$$\begin{cases} F'(t) + \phi(t) - \psi(t) = f'(t), \\ F'(t)/t - F(t)/t^2 + \phi(t)/t - \psi(t)/t = 0 \; ; \end{cases}$$

whence

$$\begin{cases} F(t) = tf'(t) = Bt - Ct^2, \\ \phi(t) - \psi(t) = tf''(t) = Ct. \end{cases}$$

This really contains the whole of thermoelectric theory without any reference to local differences of potential, but only to electromotive force round a complete circuit. But when we come to the question of difference of potential within the substance at different parts of the circuit, we find that according as we treat it in one or the other of the following ways we may leave the difference of potential at the junctions indeterminate and free to be settled in accordance with hypotheses which may be found convenient in electrostatics, or we find it determined for us, and must make our electrostatic hypotheses accord therewith.

The first way is that of Thomson, as I understand it.
Assume that there is no thermoelectric difference of potential
between parts of the same metal at different temperatures,
at all events till electrostatic experiments shall show that there
is.   It follows that we must assume that the passage of
electricity between two points at different temperatures must
cause a conveyance of energy to or from the region between
those points by some other means than by passage from one
potential to another.   Such conveyance of energy may be
very properly likened to the convection of heat by fluid in a
tube, for although convection is in general dissipative, it is
not necessarily so, *e. g.* a theoretically perfect regenerator.
Suppose, then, that in metal X unit of electricity carries with
it $\int\phi(t)dt$ of heat, and in metal Y, $\int\psi(t)dt$, this will account for
the proved transference of heat in the two metals.   When a
unit of electricity passes across a junction at temperature t
from X to Y, it must liberate at that junction a quantity of
heat $\int\phi(t)dt-\int\psi(t)dt$; but the actual effect at this junction
is that heat $F(t)$ disappears ; hence the excess of potential at
the junction of Y over X must be

$$F(t)+\int\phi(t)dt-\int\psi(t)dt \quad \text{or} \quad A+Bt-\tfrac{1}{2}Ct^2,$$

A being a constant introduced in integration.   If, then, we
assume a " specific heat of electricity," the actual difference
of potential at a junction may contain a constant term of
any value that electrostatic experiments indicate.

But the facts may be expressed without assuming that
electricity conveys energy in any other way than by passing
from a point of one potential to a point of different potential.
This method must be adopted by those who maintain that the
Peltier effect measures the difference of potential between two
metals in contact.   *Define* that if unit-electricity in passing
from A to B points in a conductor homogeneous or hetero-
geneous does work, whether in heating the conductor, chemical
changes, or otherwise, the excess of potential of A over B
shall be measured by the work done by the electricity.   This
is no more than defining what we mean by the potential
within a conductor, a thing we do not need to do in electro-
statics.   This definition accepted, all the rest follows.   Be-
tween two points differing in temperature dt the rise of
potential is $\phi(t)dt$ in X, $\psi(t)dt$ in Y ; at the junction the
excess of potential of Y over X is $F(t)=Bt-Ct^2$.

The second method of arranging one's ideas on this subject
has the advantage that it dispenses with assuming a new pro-
perty of that hypothetical something, electricity ; but there
is nothing confusing in the first method.

<div align="center">2 B 2</div>

II. The thermodynamics of the voltaic circuit may be dealt with on either method of treatment ; in the equations already used, instead of speaking only of the heat disappearing from any region, we have to consider the heat disappearing when the unit electricity passes plus the energy liberated by the chemical changes which occur. Consider a thermoelectric combination in which there is chemical action at the junctions when a current passes.

If Gt be the function of the temperature which represents the energy of the chemical reaction which occurs when unit of electricity passes from X to Y across the junction, we have

$$F(t_2) + G(t_2) - F(t_1) - G(t_1) + \int_{t_2}^{t_1} \psi(t)\,dt + \int_{t_1}^{t_2} \phi(t)\,dt = f(t_2) - f(t_1),$$

$$F'(t) + G'(t) + \phi(t) - \psi(t) = f'(t),$$

$$F'(t)/t - F(t)/t^2 + \phi(t)/t - \psi(t)/t = 0 ;$$

whence

$$\left. \begin{aligned} F(t) &= tf'(t) - tG'(t), \\ \phi(t) - \psi(t) &= t\{f''(t) - G''(t)\}. \end{aligned} \right\}$$

If now we proceed on the hypothesis of specific heat of electricity, we are able to make the differences of potentials at the junctions accord with the indications of electrostatic experiments. We are, then, by no means bound in a voltaic cell to suppose that there is a great difference of potential between the electrolyte and the metal because there is a reaction there, for we may suppose the energy then liberated is taken up by the change that occurs in the specific heat of electricity.

III. Adopting the second method of expressing the facts, we may consider further the location of the difference of potential in a voltaic cell. In the case of a Daniell's cell consisting of Cu | $CuSO_4$ | $ZnSO_4$ | Zn, at which junction is the great difference of potential? Dr. Lodge places it at the junctions of the metals and the electrolytes. For this there is really some experimental reason, but without such reason it is not apparent why there may not be a great difference of potential between $CuSO_4$ and $ZnSO_4$. In that case, in an electrolytic cell with zinc or copper electrodes and $ZnSO_4$ or $CuSO_4$ as electrolyte there would exist a small difference of potential between the metal and the electrolyte. Take the latter case, an electrolytic cell of $CuSO_4$, and let us leave out of account the irreversible phenomena of electrical resistance and diffusion. First, let us assume, as is not the fact, that the only change in the state of the electrolytic cell when a current has

passed is addition of copper to one plate, loss of copper from the other plate ; what could be inferred ? Imagine a region enclosing the anode, when a current has passed, what changes have occurred within the region ? An equivalent of copper has disappeared from the anode, and that same quantity of copper has departed and gone outside the region. But by our supposition, nothing else has happened barring increase of volume for liquid by diminished volume of metallic copper ; there is no more and no less $CuSO_4$ in the region, the same quantity therefore of SO_4. All the work done in the region is to tear off a little copper from the surface of the anode and to remove it elsewhere. If the fact were as assumed it would follow that the passage of the current did little work in the passage from copper to sulphate of copper, and consequently that the difference of potential between the two is small. But the fact is, other things happen in the cell than increase of the kathode and diminution of the anode. In contact with the anode there is an increase of $CuSO_4$, in contact with the kathode $CuSO_4$ disappears : this is a familiar observation to every one. Reconsider the region round the anode. Assume as another extreme hypothesis that after a current has passed we have in this region the same quantity as before of copper, but more $CuSO_4$; SO_4 has entered the region and has combined with the copper. A large amount of energy is therefore brought into the region, which can only be accounted for by supposing that the electricity has passed from a lower potential in the copper to a higher potential in the electrolyte. The legitimate conclusion is, then, that there is between Cu and $CuSO_4$ a difference of potential corresponding to the energy of combination ; and the basis of the conclusion is the simple observation that the copper is dissolved off one plate but remains in its neighbourhood, whilst it is precipitated on the other plate, impoverishing the solution. In other words, it is the SO_4 that travels, not the Cu.

Now consider the ordinary Daniell's cell. Is there a substantial difference of potential at the junction of $CuSO_4$ and $ZnSO_4$? Is there, in fact, a difference apart from the Peltier difference ? Imagine a region enclosing the junction in question ; it might have been that the effect of a current passing was to increase the zinc and diminish the copper by an equivalent of the electricity which passed, from which we should have inferred that the seat of the electromotive force in a Daniell's cell was at the junction of the two solutions. But it is more nearly the fact that no change whatever occurs in the region in question when a current passes, and that all that

happens is that a certain quantity of SO_4 enters the region and an equal quantity departs from it, from which follows that there is no potential difference, other than a Peltier difference, at this junction.

Neither of the extreme suppositions we have made as to concentration or impoverishment of the solution is in fact true, but they serve to show that the position of the steps in potential depends entirely on the travelling of the ions. The fact is, that in general both ions travel in proportions dependent on the condition of the electrolytes ; it is probable that the travelling of the SO_4 depends on some acidity of the solution.   Given the proportion in which the ions travel and the energy of the *reversible* chemical reaction which occurs, and we can calculate the differences of potential at the junctions.

In the preceding reasoning an assumption has been made, but not stated.   It has been assumed that the passage of a current in an electrolyte is accompanied by a movement of ions only, and not by a movement of molecules of the salt; that is, when unit of electricity passes through a solution of $CuSO_4$, xCu travels in one direction and $(1-x)SO_4$ in the opposite direction, but that $CuSO_4$ does not travel without exchanges of Cu and of SO_4 between the molecules of $CuSO_4$. In the supposed case when there is no concentration around the anode, my assumption is that Cu is dissolved off the anode, and that an equal quantity of Cu leaves the region around the anode *as Cu* by exchanges between the molecules of $CuSO_4$. But it is competent to some one else to assume that in this case SO_4 *as SO_4* enters the region by exchanges between the molecules of $CuSO_4$, and that at the same time a molecule of $CuSO_4$ leaves the region without undergoing any change. Such a one would truly say that there was no inconsistency in his assumption; and that if it be admitted, it follows that the difference of potential at the junction $CuSO_4$ | Cu is that represented by the energy of the reaction.   I prefer the assumption I have made, because it adds nothing to the ordinary chemical theory of electrolysis; but it is easy to imagine that facts may be discovered more easily expressed by supposing that an electric current causes a migration of molecules of the salt, as well as a migration of the components of the salt.

XXXIX. *A Comparison of the Standard Resistance-coils of the British Association with Mercury Standards constructed by M. J. R. Benoit of Paris and Herr Strecker of Würzburg. By* R. T. Glazebrook, *M.A., F.R.S., Fellow and Assistant Tutor of Trinity College, Cambridge*[*].

IN accordance with the resolution of the Electrical Congress held in Paris in 1884, the Electrical-Standards Committee of the British Association decided to have made a series of resistance-coils in terms of the Legal Ohm; and the work of testing and comparing these coils was entrusted to me. In Paris, at the request of the Minister for the Post Office and Telegraphs, M. J. R. Benoit undertook the same task. An account of his experiments is published in the *Journal de Physique* for January 1885.

M. Benoit started *ab initio*, and constructed a series of glass tubes, the electrical resistance of which, when filled with mercury, can be calculated from their dimensions. Four of these were made, each having a resistance of about 1 ohm.

The plan adopted by the Committee was different. The specific resistance of mercury in terms of the British-Association unit has been carefully determined by Lord Rayleigh and others.

For the purpose of constructing Legal Ohms, it was decided to adopt a number for this quantity founded on their experiments, and then work from the British-Association standards. To adopt the other course would only have been to repeat at some trouble the experiments of Lord Rayleigh, M. Mascart, Herr Strecker, and others.

M. Benoit made a number of copies of his mercury-standards, and after reading his paper, I wrote and asked him to send me one or more of these, that I might compare them directly with the coils which had by that time been constructed for me by Messrs. Elliott Bros. M. Benoit replied most courteously, and sent me, about Easter, three of his copies. The object of the present paper is to give an account of the comparison of these with the standards belonging to the British Association.

M. Benoit's copies were mercury-standards. Each consisted of a glass tube bent several times, A A, fig. 1. The ends of this tube are ground flat and pass into two glass cups, B, B, which for most of their length are considerably wider than the tube, but taper down at their lower ends. The tubes are connected to the cups by short bits of india-rubber tubing,

C, C, which fit tightly over the narrow ends of the cups, and
are secured by wrapping string firmly over the india-rubber.

Fig. 1.
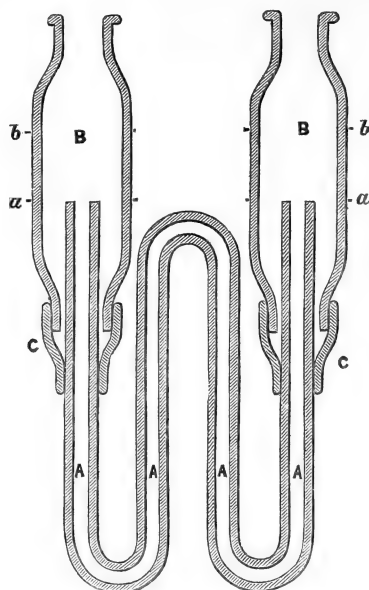
To make the joint tight the india-rubber and glass were var-
nished over with shellac varnish. The cups open at the top,
and can be closed by glass stoppers.

The standards were accompanied by full directions for use.
I give a free translation of the greater part of the instructions.

1. On each of the cups are engraved two marks $a\,a$, $b\,b$.
The lower mark $a\,a$ indicates the position which the extremity
of the tube introduced into the cup ought to occupy. The
upper mark $b\,b$ indicates the top of the mercury in the tube
when filled. These two conditions must be fulfilled approxi-
mately; an error of ·5 centim. in their sum changes the
resistance either way by about ·00018 ohm.

2. *Method of Filling.*—The tube may be filled in air in the
following manner:—Place it nearly horizontally and pour
some mercury into one of the cups; then incline it gradually,
shaking it a little, until the mercury enters the tube. The
mercury should fill the tube slowly, without leaving a trace of
air. Add mercury always by the same cup until it reaches
the upper mark $b\,b$ in both cups. The method is not always
successful; it is better to work in a vacuum.

[Various methods for doing this are possible; it is perhaps
hardly necessary to give the details of the one employed by
M. Benoit.]

3. *Method of Using the Standard.*—The standard is introduced into the circuit by means of contact-pieces dipping into the mercury in the cups. These pieces should not reach more than a few millimetres below the surface. Contact-pieces of amalgamated copper cannot be used, because they render the mercury impure and alter its resistance rapidly, diminishing it appreciably in a few hours. Platinum, again, does not make a constant contact with the mercury; and the uncertainty produced by its variability is fatal to its use. To avoid this double difficulty, M. Benoit employed contact-pieces of a special form (fig. 2). A glass tube A is drawn out to a point at its lower end; through this point a platinum wire B passes. The wire is held in position by shellac C; and a small cup D of thin glass is attached to its lower end also by shellac. Thus the two separate glass portions A and D are in electrical communication by means of the platinum wire B. The two portions A and D are filled with mercury in a vacuum. The mercury is thus brought into good contact with the platinum, and the mercury-platinum contact remains unchanged during the observations. Into the upper division A one end of a stout copper rod E is plunged; the other end of this rod forms the connection with the rest of the circuit. The cup D dips a few millimetres below the mercury in the standard. The mercury which fills it remains constantly in contact with the platinum wire, and may be kept without

Fig. 2.

change almost indefinitely. These contact-pieces introduce an appreciable resistance of 2 to 3 thousandths of an ohm into the circuit ; but this resistance remains constant, and can be eliminated by a method of substitution.
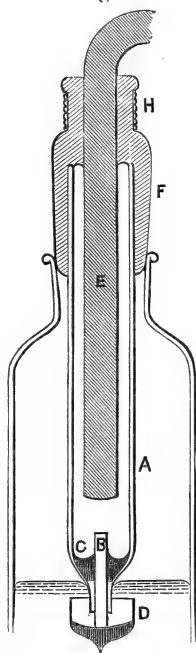
The standard is supported in a glass vessel, and can be reduced in temperature to zero by filling the vessel with finely-broken ice. The values of the standards are given at zero. The value at any other temperature is given by the formula

$$R_t = R_0(1 + \cdot0008649t + \cdot00000112t^2),$$

t being the temperature in degrees Centigrade.

4. *Preparation of the Mercury.*—The mercury may be purified by the action of nitric acid, and dried by means of sulphuric acid and caustic potash.

Experiment showed that mercury from different sources, even when it had been rendered impure by the admixture of copper, lead, or zinc, after being treated by this process, gave the same results. The process, however, does not free the mercury from silver or from the less oxidizable metals.

[In my experiments described below the mercury was freshly distilled by the aid of the admirable piece of apparatus designed by Weinhold, and introduced into England by Mr. W. N. Shaw.]

5. *Method of Cleaning the Tubes*.—The tubes should be cleaned by passing through them in succession:—

1. Distilled water.
2. Strong nitric acid.
3. Distilled water.
4. Ammonia.
5. Distilled water.

They must then be dried by a current of dry air.

To clean the tubes it is best to separate them from the cups. To effect this, the pieces of india-rubber tubing which connect them should be cut. To make the glass slip into the india-rubber tubing, it should be moistened with a drop of benzine.

In preparing the tubes for my measurements, I endeavoured to carry out the above instructions as carefully as possible. The resistance comparisons were made by Carey Foster's method, using the wire bridge of the British Association as designed by Dr. Fleming.

In order to compare the resistance of one of the tubes with a standard coil, it was necessary either to know accurately or to eliminate the resistance of the contact-pieces. It was also important to determine within what limits the resistance of the contact-pieces remained constant, and whether they could be repeatedly filled with mercury in such a way as to retain the same resistance.

For this purpose they were compared with a short piece of copper rod. The cups D (fig. 2), one belonging to each contact-piece, were immersed in the same beaker of mercury, being placed close together and covered to the same depth as when actually in use; the other ends of the copper rods E connected in the usual way to the bridge. The contact-tubes had been filled by being placed in a large test-tube which was exhausted, and into which mercury was then admitted by means of a tap attached to the test-tube. The resistance of the contact-pieces was thus found in terms of the divisions of the bridge-wire before and after a set of comparisons of the mercury-tubes and standard coils.

It was found that the resistance of the contact pieces remained very nearly constant during the time occupied in making a series of comparisons. The variations in the values found before and after rarely amounted to more than 1 bridge-wire division, or about ·00005 ohm ; and the mean of the two values obtained is pretty certainly correct to less than this.

At the same time different fillings of the same contact-tubes led to very different values for their resistances. This was no doubt due to small irregularities in the contact between the platinum and the mercury. Thus I found the following values in terms of a bridge-wire division :—

Date &c.	Resistance of contacts.
March 25	93·4 b.w.d.
„ Contacts refilled	69·4 „
„ 26 { Copper rods being left in the mercury overnight .... }	68·2 „
„ „ Contacts refilled, one renewed	114·5 „
„ 28 Copper rods being left in since 26th...	109·4 „

The differences between the 69·4 and the 68·2, and, again, between the 114·5 and 109·4, are due, I believe, to the copper of the contact-rods being dissolved by the mercury in the tubes.

On March 28th, the contact-tubes were cleaned and refilled, and the resistance was found to be 57·2 b.w.d. Throughout the experiments until April 9, when one of them was broken, their values did not differ greatly from the above.

On April 11th, new contact-tubes were prepared and used throughout the rest of the experiments; their value remained fairly constant at about 58 b.w.d.

Thus the quantity actually determined by the observations was the difference between the resistance of the mercury tube + the contact pieces and the standard coil. In order to get the resistance of the mercury tube in terms of the standard coil, the resistance contact-pieces found as above described had to be subtracted.

Another way of eliminating the resistance of the contacts from the result is to compare first the mercury tube and then the standard with some other coil, using the same contact-pieces to connect the mercury tube and the standard to the bridge. This can be done by removing the contact-tubes from the mercury tube, and dipping them into two mercury cups, into which the electrodes of the standard also dip. Since,

however, my apparatus allowed me to measure the resistance of the contact-tubes with all the accuracy I desired, the first method was the more convenient, as it necessitated fewer observations.

The comparisons were made both with the original standards of the British Association—B.A. Units—and also with the Legal-Ohm Standards of the same, recently constructed for me by Messrs. Elliott Bros., taking as a basis the value for the resistance of mercury in terms of the B.A. unit adopted by the British-Association Committee. According to this,

$$1 \text{ Legal Ohm} = 1 \cdot 0112 \text{ B.A.U.}$$

The three mercury tubes Nos. 37, 38, 39, sent by M. Benoit, were compared. Between two observations of resistance the mercury was occasionally drawn through the tubes by connecting the cups alternately to the air-pump. I hoped in this manner to displace any very small air-bubble or particle of dust which might have got lodged in the tube. In the final set of observations recorded below, it will be seen that no appreciable change in the resistance was detected by this precaution. I therefore suppose the tubes to have been properly filled.

In some earlier observations, which will be referred to again shortly, variations of considerable amount were produced by passing the mercury through. In the tables below the values of the resistances which were found by comparison with the B.A.U., and reduced to Legal Ohms by means of the known relation between the two, are denoted by an asterisk.

TABLE I.

Tube No. 37. Value given by Benoit, 1·00045.	
Date and Method of Treatment.	Value in L. Ohms.
April 13, 10 A.M.	·99991*
„ 10.30	·99987
„ 11.55	·99998
„ 1 P.M. { After passing the } { mercury through. }	·99997
April 14	·99998
April 14 ...... { After passing the } { mercury through. }	·99996
April 15	·99979
April 15	·99976*
Mean value....................	·99990

TABLE II.

Tube No. 38. Value given by Benoit, 1·00066.	
Date and Method of Treatment.	Value in Legal Ohms.
April 8, 11.45 A.M.	1·00006
April 8, 1.30 A.M.	1·00018
April 9	1·00023*
April 9	1·00019
April 11 { Tube taken to pieces, re- cleaned and refilled. }	
April 13	1·00011*
April 13	1·00010
April 14	1·00015
April 15	1·00002
April 15	1·00003*
Mean value...........................	1·00012

TABLE III.

Tube No. 39. Value given by Benoit, ·99954.	
Date and Method of Treatment.	Value in Legal Ohms.
April 14	·99905
April 15, 10.30 A.M.	·99917
April 15, 11 A.M. { After passing the mercury through. }	·99921
April 15, 11.55 A.M.	·29921
April 15, 12.15 { After passing the mercury through. }	·99921
April 15	·99917
Mean value.....................	·99917

Thus we may collect the results as below.

TABLE IV.

No. of Tube.	Value found by Benoit.	Value found by R. T. G.	Difference.
37.........	1·00045	·99990	·00055
38.........	1·00066	1·00011	·00055
39.........	·99954	·99917	·00037
Mean......	1·00022	·99972	·00050

Thus there is a difference of ·0005 legal ohm between the two. My results are based upon the value of the resistance of mercury in terms of the B.A. unit adopted by the British-Association Committee. If we denote by M the resistance at 0° C. of a column of mercury 1 metre long, 1 square millim. in section, then, according to the number adopted by the Committee,

$$\text{M.} \quad = \cdot 9540 \text{ B.A.U.}$$
$$\text{B.A.U.} = 1\cdot 04820 \text{ M.}$$

The most recent values actually found for these relations are given below:—

<center>TABLE V.</center>

M in B.A.U.	B.A.U. in M.	Observer.
·95412	1·04808	{ Rayleigh * and Sidgwick.
·95374	1·04851	{ Mascart†,Nerville, and Benoit.
·95334	1·04894	Strecker ‡.
·95411	1·04809	L. Lorentz §.

M. Benoit has not compared his tubes directly with the B. A. units. The mean of my comparisons gives for his mercury tubes,

$$\text{M.} \quad = \cdot 95348 \text{ B.A.U.}$$
$$\text{B.A.U.} = 1\cdot 04878 \text{ M.}$$

Thus there is a difference of ·0005 ohm between standards issued by M. Benoit as representing the legal ohm, and those issued by myself on behalf of the B. A. Committee, M. Benoit's standards being less than mine by that amount.

Some other points remain to be noticed. The first time that I filled Nos. 37 and 39, I obtained results for the resistances differing appreciably from those given above. They were filled each time with equal care, the mercury had been treated in the same manner, and there seemed no reason, taking each observation separately, why one should be better than the other. For No. 37 I found on April 8th the value 1·00044 legal ohms ; I noticed on April 9 that this had gone up to 1·00071 ; and on passing the mercury through as already described, it rose further to 1·00080. These differences are considerably greater than any possible errors of observation ;

* "On the Specific Resistance of Mercury," Phil. Trans. pt. 1, 1883.
† *Journal de Physique*, June 1884.
‡ *Abh. der bayer. Akad.* Bd. xv.; also Wied. *Ann.* vol. xxv.
§ Wied. *Ann.* vol. xxv.

and it was clear that there was some small change progressing in the tube. It was carefully examined, but no trace of an air-bubble could be seen ; and then it was emptied, cleaned again, and refilled, with the results given in Table I. Much the same was observed with coil No. 39. No. 38 was cleaned and filled twice, but gave perfectly consistent results all through. This uncertainty seems to me to constitute one serious objection to the general employment of mercury tubes as standards.

I believe that for the observations recorded in the above Tables the tubes were properly filled, and that there were no bubbles of air in them. This, I think, is shown by the agreement between the results of different fillings, and I suppose that the resistance will not seriously alter so long as the same mercury remains in the tubes ; but it appears that, after filling, electrical experiments are required to make certain that every bubble of air has been removed, and that the tube really has its true resistance. I should imagine, too, that the tubes would require somewhat frequent refilling to make sure that the mercury may remain pure. My experiments showed that it was almost impossible to keep the inside of the cups above the mercury perfectly dry. It was necessary, when making the comparisons, to remove the glass stopper and insert the contact-pieces; and this had to be done when the tube was immersed in the ice-water.

The cups were open to the air for a short time in making this change, and that short time was quite sufficient to cause a deposit of dew to be formed on the inside of the cup. So long as this slight moisture remained in the cup and did not reach the tube itself, of course it did not affect the results ; but it would be difficult to feel certain that after a time the mercury in the tube was quite dry.

This difficulty would be avoided by working at the temperature of the room rather than at that of melting ice. The large temperature-coefficient of mercury, from three to four times that of platinum-silver alloy, is, however, an objection to this.

Another difficulty, caused by the necessity of working at zero, was that the mercury in the cups was always slightly warmer, $0°\cdot2$ or $0°\cdot3$ C., than the ice. This was, no doubt, caused by the conduction of heat down the copper connecting-rods, and from the upper portions of the glass of the cups which were exposed to the air. This, of course, would necessitate a small correction to the values of the resistances given in the Tables; but the correction must be exceedingly small, for the temperature of the mercury in the tube itself, where it is actually in contact with the ice, must be zero,

and it is only the small portions of the tubes which lie within
the cups which will be at the higher temperature.

The necessity of using the somewhat complicated con-
necting pieces is also a great drawback to the practical use-
fulness of the mercury standards. I hope shortly to carry
out some experiments on the permanence of the contact be-
tween mercury and amalgamated platinum. Contact-pieces of
platinum with their end amalgamated with mercury would
be easier to work with, and should give consistent results.

I have also made some observations on the variation of the
resistance of mercury with temperature.

The formula quoted above from Benoit is given by Mascart,
Nerville, and Benoit as determined from experiments between
0° and 100°.

It is
$$R_t = R_0(1 + \cdot0008649t + \cdot00000112t^2).$$

According to Strecker,
$$R_t = R_0(1 + \cdot000900t + \cdot00000045t^2).$$

This is derived from observations at 0°, 10°, 15°, and 20°.

Lorenz finds that between 0° and 27°·32 his experimental
results agree with the formula
$$R_t = R_0(1 + \cdot0009013t);$$

and from 8°·32 to 35°·31 with
$$R_t = R_0(1 + \cdot000916t).$$

While Siemens and Halske give
$$R_t = R_0(1 + \cdot0008523t + \cdot000001356t^2).$$

I made observations on the two tubes, Nos. 37 and 39,
determining their resistances at temperatures of about 0°, 5°,
10°, and 15°; and the results of the observations show that the
average change for low temperatures is less than that given
by the above formulæ. Thus, if we call $(R_t - R_0)/R_0t$ the
average change between temperatures t and 0, the values, as
found from my experiments and as calculated by the formulæ
of Siemens and Benoit, are as given below.

Average change between	Siemens and Halske.	Benoit.	R. T. G.
5 and 0	·000858	·000870	·000834
10 „ 0	·000865	·000876	·000861
15 „ 0	·000872	·000881	·000879

The values given in the last column are the mean of those derived from the two tubes; the greatest difference between the mean and any one observed value was ·000005. Strecker's values would be above Benoit's.

Lord Rayleigh found for the average change between 0° and 12°, ·000861.

Of course the value of this temperature-coefficient depends somewhat on the glass of the tube; but the differences between the coefficients of expansion of various kinds of glass are too small to account for the whole of the differences shown above.

The paper by Herr Strecker on the same subject has been already referred to, and it will be noticed that the number he arrives at as expressing M. in B.A. units differs by ·00078 from that given by Lord Rayleigh ; or, if we take the numbers expressing the B.A.U. in terms of M., the difference is ·00086. Now Strecker had compared his mercury tubes with a B.A.U. tested carefully by myself against the standards, and found to have the value of

·99937 B.A.U. at 17·7.

This coil is marked �«, No. 54.

On the conclusion of his experiments, Herr Strecker returned this coil to me, and kindly sent with it a German-silver copy of his tubes marked No. 13, and said to have, according to his determinations, a resistance of

1·00189 M. at 10° C.,

with a temperature-coefficient of

·000247 per degree.

It was thus in my power to repeat my comparison of �«, No. 54, with the standards, and to compare the values of M. as found by Herr Strecker with the B.A.U. The value found for �« 54 agreed very closely with that given by Herr Strecker; the results of my comparison of Herr Strecker's coil with the B.A.U. are given below. The comparisons were made as usual, by Carey-Foster's method; but since the difference between the two resistances was such as to require the use of a long piece of the bridge-wire, a resistance of 20 B.A. units was introduced in multiple arc with the standard 1 unit. This resistance was composed of the two standard ten-unit coils of the Association.

Table VI.

Date.	Standard of Comparison.	B.A.U. in M.	M. in B.A.U.
April 9	Flat.	1·04814	·95407
„ 15	℞ 54.	1·04806	·95413
„ „	Flat.	1·04791	·95427
16	Flat.	1·04820	·95402
„ „	℞ 54.	1·04811	·95410
„ 17	℞ 54 and 20.	1·04801	·95419
,, „	Flat and 20.	1·04824	·95399
„ „	Flat and 20.	1·04797	·95422
Mean		1·04808	·95412

These numbers, it will be seen, agree with those found by Lord Rayleigh and Lorenz, and differ greatly from Strecker's values.

They represent the results of the comparison of a German-silver copy of Strecker's tubes with the B.A. units, including the actual coil employed by Strecker, ℞ No. 54; while Strecker's numbers give the result of the comparison of his tubes directly with No. 54.

I have not been able to explain the discrepancy. Herr Strecker suggests in a letter to me on the subject, that the resistance of his coil No. 13 has changed somewhat in the year which has elapsed since his comparisons were made. At present I am in correspondence with Prof. F. Kohlrausch, of Würzburg, in whose laboratory Strecker's experiments were conducted, and hope to obtain another copy of Strecker's tubes, or at any rate to have another comparison made between his tubes and the B.A. standards.

XL. *On the Accuracy of Focus necessary for Sensibly Perfect Definition.* By Lord Rayleigh, *F.R.S.**

IN my "Investigations in Optics"† I have examined the effect upon definition of small disturbances of the wave-surfaces from their proper forms. It follows, for instance,

---

* Communicated by the Author.
† Phil. Mag. 1879 & 1880.

that the aberration of a plano-convex lens focusing parallel rays of homogeneous light is unimportant, so long as the fourth power of the angular semi-aperture does not exceed the ratio of the wave-length to the focal distance $[\alpha^4 < (\lambda/f)]$, a condition satisfied by a lens of 3 feet focus, provided that the aperture be less than 2 inches. I propose at present to apply similar principles to the question of focusing.

The most convenient point of view is that explained * for calculating the focal length of lenses. If the lens AB converges parallel rays to a focus at F, the retardation of the
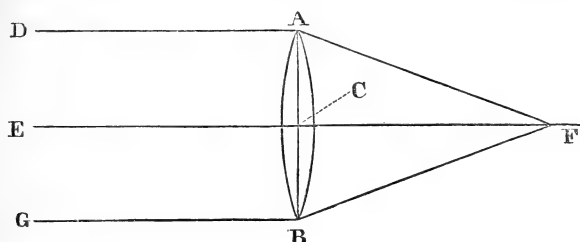
central ray E F, due to the substitution of a thickness t of glass for air, is $(\mu - 1)t$; and this must be equal to the retardation of the extreme rays passing the (sharp) edge of the lens, *i. e.* AF−CF. Thus, if AC$=y$, FC$=f$,

$$(\mu - 1)t = \sqrt{(f^2 + y^2)} - f = \frac{1}{2}\frac{y^2}{f}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

approximately, which gives the focal length in terms of the semi-aperture and the " thickness " of the lens.

If we suppose that μ varies,

$$\delta\mu \cdot t = -\frac{1}{2}\frac{y^2}{f^2}\,\delta f, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

giving the change of focus required to compensate the change of μ. Let us, however, inquire what is the state of things at the old focus. The secondary rays from the extreme boundary of the lens arrive with the same phase as before the change of index; but the central ray undergoes a relative retardation amounting to $\delta\mu \cdot t$. This quantity tells us the discrepancy of phase; and we know that if it is less than $\frac{1}{2}\lambda$, the agreement of phase is still good enough to give nearly perfect definition. Hence from (2) we see that a displacement δf from the true focus will not impair definition, provided

$$\delta f < \frac{f^2\lambda}{y^2}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

* *Loc. cit.* p. 480.
2 C 2

It appears that the linear accuracy required is the same whatever the absolute aperture of the object-glass may be, provided that the *ratio* of aperture to focal length be preserved.

In some trials that I have made the diameter of the object-glass was $1\frac{1}{8}$ inch, and the focal length 12 inches. Taking $\lambda = \frac{1}{40,000}$ inch, we get from (3)

$$\delta f < \cdot 0115 \text{ inch},$$

a result which corresponded very well with observation. The instruments employed were the collimator and telescope of a spectrometer, the object under examination being a slit backed with a soda-flame. A high-power eye-piece was used, and the telescope was adjusted until the edge of the slit and the wire in the eye-piece were seen well defined together. The instrument was unprovided with an easy focusing motion, so that it was not possible to try backwards and forwards conveniently. In this way the setting corresponded more closely to the suppositions of theory than if it were the result of comparisons between appearances at equal distances within and without the point chosen. It will be understood that there is no theoretical limit to the accuracy with which a focal point may be ultimately determined, if the lenses are good, and observations are multiplied with suitable precautions to avoid asymmetry.

In ten settings the extreme difference was only ·02 inch, showing that a displacement of ·01 inch from the true focal point was just recognizable.

By using various coloured flames, or by throwing a spectrum upon the slit of the apparatus, we may determine the focal length for different kinds of light. With proper achromatic lenses the differences should be pretty small, the minimum focal length corresponding to the yellow-green rays. It so happens that my instrument is far from properly compensated, and gives a fair primary spectrum, so that the difference of focus for yellow and green is very easily recognized. In the case of a single lens this method would give the dispersive power of the glass with fair accuracy. By comparison with the theory of the resolving power of prisms, we see that the dispersion is about as favourably determined with a lens as with a prism of equal thickness. In either case a change of index such that $\delta\mu \cdot t = \frac{1}{2}\lambda$ leaves the phase agreement nearly unaltered at the original points ; but in other respects the circumstances are probably rather more favourable in the case of the prism.

It is generally considered that the most accurate way of

focusing a small telescope is to move the eye across the eye-piece, altering the adjustment until there seems to be no re-lative motion of object and cross wires. I have tried this plan in an improved form in order to see whether a higher degree of accuracy of adjustment was really attainable, al-though theory seemed to show that no great advance was to be looked for. A heavy pendulum, executing complete vibrations in about two seconds, was fitted up in front of the telescope, and carried with it a screen perforated by a slit. The width of the slit was about a quarter of the entire aper-ture, and the oscillations were at first of such amplitude as just to bring the extreme edges of the lens into play. In the earlier experiments the slit of the collimator was backed by the clouds, a piece of green glass being interposed. This was before I had discovered the remarkably unachromatic character of the instruments, and I was puzzled to interpret the ap-pearances presented. On one side of the focus the relative motion of the image was (as it should be) in the same direc-tion as that of the pendulum, and on the other side in the opposite direction; but the transition was not well defined, and the image executed evolutions very visible to the ob-server, who at the same time was not able to describe them as swinging in one direction or the other. The effect upon the eye was remarkably unpleasant and fatiguing to watch; it disappeared when recourse was had to sodium light, and doubtless depended upon the variation of quality in the light. It may be noticed that spherical aberration would show itself by a swinging of the image in a period *half* that of the pendulum.

With the soda-flame the adjustment to focus by getting rid of the swinging motion was pretty accurate; but not much advantage was gained in comparison with a setting by simple inspection under full aperture. As before, the extreme difference in a set of ten was about ·02 inch.

The substitution of white for monochromatic light was in-structive. In either extreme position of the oscillating slit the light was seen to be spread into a spectrum of moderate length, the blue and red being interchanged after each half period. Under these circumstances the cross wires can be made to maintain their position in that part of the spectrum only for which the telescope is focused. If, for example, it be the green of the spectrum, we may bring the cross wires to this position when the pendulum is at rest, and then, in spite of the oscillation, the position will be maintained. If, without altering the focus, we move the cross wires to another part of the spectrum, then, when the pendulum oscillates, the

wires will be seen on a different part of the spectrum after each half period. In order to fix the new part of the spectrum upon the cross wires, a change of focus is demanded. This experiment would hardly succeed with properly compensated object-glasses, but it could be imitated with the aid of single lenses.

XLI. *On an Improved Apparatus for* Christiansen's *Experiment. By* Lord RAYLEIGH, *F.R.S.**

THE very beautiful experiment in question, described by C. Christiansen in Wiedemann's *Annalen* for November 1884, consists in immersing glass-powder in a mixture of benzole and bisulphide of carbon of such proportions that for one part of the spectrum the indices of the solid and of the fluid are the same. Being interested in this subject from having employed the same principle for a direct-vision spectroscope (Phil. Mag. January 1880, p. 53), I have repeated Christiansen's experiment in a somewhat improved form, which it may be worth while briefly to describe, as the matter is one of great optical interest.

I must premise that the beauty of the effect depends upon the correspondence of index being limited to one part of the spectrum. Rays lying within a very narrow range of refrangibility traverse the mixture freely, but the neighbouring rays are scattered laterally much as in passing ground glass. Two complementary colours are therefore exhibited, one by direct, and the other by oblique, light. In order to see these to advantage, there should not be much diffused illumination, otherwise the directly transmitted monochromatic light is liable to be greatly diluted. The prettiest colours are obtained when the undisturbed rays are from the green; but the greatest general transparency corresponds to a lower point in the spectrum.

The improvement referred to relates merely to the use of a flat-sided bottle to contain the preparation. In order to get a satisfactory result it is necessary that the sides of the containing vessel be pretty good optically. This condition may be satisfied with a built-up cell, but on account of the difficulty of finding a suitable cement, it is rarely that such cells remain in good order for any length of time. It occurred to me that a bottle might be made to answer the purpose, provided the precaution were taken of *using the same kind of glass for the bottle and for the powder*. The *outer* sur-

---

* Communicated by the Author.

faces of the glass sides of the bottle can be worked flat, while the unavoidable irregularities of the inner surfaces are compensated by the liquid, which, being adjusted to have the same index as the powder, will have also the same index as the glass of the bottle.

The bottles that I have used* are about 3 inches high, $1\frac{1}{2}$ inch wide, and about $\frac{3}{4}$ inch thick, outside measurement. The outer surfaces are worked (like plate glass), and not merely flattened upon a wheel, as is usual with ordinary perfume bottles. For my earlier trials I was provided with a piece of flint glass from the same pot as the bottles; but although the experiment succeeded well enough as regards the elimination of the internal irregularities of the walls, the glass-powder itself did not behave as well as I had seen plate-glass powder do. It appeared ultimately that the flint was not sufficiently homogeneous for the purpose, and another specimen of flint was also a partial failure, from the same cause; but a sample of optical flint, kindly supplied to me by Dr. Hopkinson, gave excellent results.

It is more important that the powder should be homogeneous in itself than that it should correspond very accurately with the glass of the bottle. For ordinary purposes plate-glass powder (all, of course, from one piece) may be used in a bottle of soda-glass, or even of ordinary low flint. In preparing the powder great care is required to exclude dirt. With respect to the coarser grades there is no great difficulty, but the finer powder is apt to be contaminated with the substance of the mortar. I prefer to use one of iron, so that a magnet will remove the foreign matter. The elimination of fine dust is also facilitated by a blast of wind from bellows.

In order to get good definition it is necessary not only that the powder be homogeneous, but that the temperature be uniform; for, as Christiansen has shown, the transmitted ray rises rapidly in refrangibility with temperature. In order to secure homogeneity it is sometimes necessary to shake up the preparation, which (to prevent the formation of air-bubbles) is best done with a rather gentle motion while the bottle is held nearly horizontal. The proportion of liquids necessary varies with the temperature and with the kind of glass. Flint will require a higher proportion of bisulphide of carbon than plate-glass. If the transmitted light is too high in the spectrum, add more bisulphide of carbon; if too low, more benzole.

The experimenter, working in a room lighted in the ordinary manner, will be disposed at first to underrate the degree

* Supplied by Messrs. Harvey and Peak, Beak Street, Regent Street.

of homogeneity of the transmitted light. If the shutters be nearly closed, so that light finds entrance through a narrow slit only, a better judgment can be formed, which may be tested by prismatic analysis.

In an otherwise dark room, lighted by a powerful soda-flame, it is interesting to remark how very slight a change in the critical colour manifests itself in the general appearance of surrounding objects seen through the preparation. When the ray of maximum transmission corresponds closely to that of soda, the powder is almost invisible, and objects are seen as through a clear medium. But so slight a change of temperature brings with it a hazy appearance, that it requires some care to obtain the best effect. It is desirable also to exclude by absorbing media the blue light which usually attends a soda-flame in very sensible degree.

XLII. *Optical Comparison of Methods for observing Small Rotations.* By Lord Rayleigh, *F.R.S.*[*]

IN order to measure very small rotations, *e. g.* of the suspended parts of a galvanometer or magnetometer, two methods are commonly employed. We may either observe with a magnifier the motion of a material pointer; or, following Gauss, cause the rotating parts to carry round a mirror in which a scale is seen by reflection. In a modification of Gauss's method, well known from Sir W. Thomson's galvanometers, the image of a dark or bright line is thrown objectively upon the scale. In deciding which arrangement to adopt in any particular case, various circumstances would have to be taken into account, but still a comparison of capabilities from a purely optical point of view is not without interest.

In the mirror method the optical limit depends upon the horizontal breadth of the mirror itself. The easiest road to the desired conclusion, as well as the most instructive, is by a direct application of the principles of the wave theory. To take the simplest case, we will suppose the mirror rectangular. Consider, then, a luminous point, and its image after reflection, whether in the focal plane of a telescope, or formed directly upon a scale. The optical work being perfect, the secondary rays from every part of the mirror agree in phase at the focal point. Now suppose that the mirror rotates through such an angle that one vertical edge advances a quarter of a wavelength ($\frac{1}{4}\lambda$), while the other retreats to the same amount, and consider the effect on the phase-relations at the point in ques-

tion. It is evident that one extreme wave is accelerated and the other retarded by $\frac{1}{2}\lambda$, and that the phases are now distributed uniformly over a complete cycle. The result is therefore darkness; and the effect of the rotation has been to shift the image through half the width of the central bright band which, with accompanying fringes, is the representative in the image of a mathematical line [*]. Such a motion would be visible (with proper arrangements as to magnifying), but the limits of revolving power are being approached. It is to be noticed that the conclusion is independent of the focal length of the mirror and of the employment of a telescope. Provided of course that the full width of the mirror is really used, a motion of its vertical edges through $\frac{1}{4}\lambda$ may be made evident.

A comparison with the method by direct observation of a pointer is now easy ; for, as has been proved by the researches of Abbe and Helmholtz, a motion of $\frac{1}{4}\lambda$ may be rendered evident in a very similar degree by direct application of a perfect microscope to the moving object. If, therefore, we suppose the length of the pointer to be equal to the half-width of the mirror, the two methods are optically upon a level. It is needless to say that it would be easy to give the pointer a great advantage in this respect ; but the direct use of the microscope would often be interfered with by motions in the line of sight, making it impossible to preserve the focus. And besides this, it is sometimes necessary for the observer to remain at a distance.

XLIII. On the Thermodynamic Efficiency of the Thermopile. By Lord RAYLEIGH, F.R.S.[†]

DURING the last few years the thoughts of many electricians have turned to the question of the possibility of replacing the dynamo by some development of the thermopile; and it is, I believe, pretty generally recognized that the difficulty in the way is the too free passage of heat by ordinary conduction from the hot to the cold junction. The matter may perhaps be placed in a clearer light by an actual calculation, accompanied by a rough numerical estimate applicable to the case of German silver and iron.

If t, t_0 denote the temperatures of the hot and cold junctions respectively, e the electromotive force per degree Centigrade, the whole electromotive force for n pairs in series will

---

[*] See " Investigations in Optics," Phil. Mag. 1879–1880.
[†] Communicated by the Author.

be represented approximately by
$$ne(t-t_0).$$

The magnitude of the current (C) is found by dividing this by the sum of the internal and external resistances (R_0+R); and the useful work done externally per second is RC^2. It reaches a maximum when the external resistance is equal to the internal; and its amount is then
$$\frac{n^2e^2(t-t_0)^2}{4R_0}.$$

The value of the internal resistance R_0 depends upon the dimensions and specific resistances of the bars. Denoting the latter quantities by r_1, r_2, and taking σ_1, σ_2 to represent the areas of section, the common length being l, we have
$$R_0=nl\left(\frac{r_1}{\sigma_1}+\frac{r_2}{\sigma_2}\right);$$

so that the external work per second is
$$\frac{ne^2(t-t_0)^2}{4l\left(\dfrac{r_1}{\sigma_1}+\dfrac{r_2}{\sigma_2}\right)}.$$

We will now compare this with the work dissipated by ordinary conduction of heat along the bars.

If Q be the amount of heat conducted by the n pairs, r_1', r_2' the *thermal* resistances, then
$$Q=n\left(\frac{\sigma_1}{r_1'l}+\frac{\sigma_2}{r_2'l}\right)(t-t_0).$$

The fraction of this heat, supplied at temperature t, which might be converted into work by a perfect engine working between the absolute temperatures t and t_0, is $(t-t_0)/t$; so that the work dissipated per second is
$$\frac{nJ(t-t_0)^2}{t\,l}\left(\frac{\sigma_1}{r_1'}+\frac{\sigma_2}{r_2'}\right),$$

where J denotes the mechanical equivalent of heat.

The ratio of this to the useful work is
$$\frac{4J}{te^2}\left(\frac{r_1}{\sigma_1}+\frac{r_2}{\sigma_2}\right)\left(\frac{\sigma_1}{r_1'}+\frac{\sigma_2}{r_2'}\right),$$

independent of $(t-t_0)$, of n, and of l. It is further evident that the ratio in question does not depend upon the absolute values of the sections, or of the electrical and thermal resistances, but only upon the *ratios* of these quantities. Thus the *efficiency* of the thermopile is independent of the absolute

dimensions of the bars, and even of the difference of tempe-
ratures at the junctions. The *power* is increased by dimi-
nishing the length and increasing the sections to a limit not
indicated by these expressions (in which the terminal tempe-
ratures are regarded as given), and probably determined in
practice by the necessity of conveying the heat to the scene
of action.

The resistances being given, the ratio of sections σ_2/σ_1 is
to be determined so as to make our ratio a minimum. This
happens when

$$\left(\frac{\sigma_2}{\sigma_1}\right)^2 = \frac{r_2 r_2'}{r_1 r_1'};$$

and thus we get

$$\frac{4\mathrm{J}}{te^2}\left(\sqrt{\frac{r_1}{r_1'}} + \sqrt{\frac{r_2}{r_2'}}\right)^2.$$

To turn this into numbers for the case of German silver
and iron, we have the following approximate numbers in C.G.S.
measure*:—

$$r_1 = 2\cdot0 \times 10^4, \qquad r_1' = 1\cdot0 \times 10^1,$$
$$r_2 = 1\cdot0 \times 10^4, \qquad r_2' = 5\cdot0 \times 10^0,$$
$$e = 3\cdot0 \times 10^3.$$

The value of J is $4\cdot2 \times 10^7$, and for t we will assume 500
(absolute measure). The use of these gives, as the ratio of
the work that would be obtained by a perfect engine from the
conducted heat to that actually obtained from the thermo-
electric force, the number 300; from which we may conclude
that the steam-engine and dynamo are not likely to be super-
seded by a German-silver and iron thermopile, even though
considerable allowance be made for the admitted roughness of
the numerical estimate.

As regards other materials, it is interesting to note that the
ratio contains as divisor the *square* of the electromotive force
per degree.

XLIV. *Electro-optic Action of a Charged Franklin's Plate.*
By JOHN KERR, *LL.D., Free Church Training College,*
Glasgow †.

I HAVE examined this difficult subject in several sets of
experiments, the last of which was finished about three
years ago. Having satisfied my own mind, I dropped the
subject, thinking that no publication of the results was

* Everett's 'Units and Physical Constants'; Landolt's *Tabellen.*
† Communicated by the Author.

required ; but on looking into M. Wiedemann's treatise, now in course of publication, I have been led to believe that a short paper on the subject may be of some use.

In his opening remarks on Électro-Optics *, M. Wiedemann draws attention to the experiments tried on Franklin's plates by MM. Quincke, Gordon, Mackenzie, and Grassman ; and he seems to accept the absence of effect in these experiments as decisive of the question of action or no action, in a uniformly charged plate of glass. Accordingly, when he comes to the earliest known instance of electro-optic double refraction (the effect of intense electric stress at the centre of a block of glass, which I discovered in 1875), he introduces my experiment as an example of a *non-uniform* and *optically active* electric field, in contrast with those other experiments †, as examples of a field sensibly *uniform* and *optically inactive*. Afterwards, at the end of his exhaustive account of the whole subject, M. Wiedemann returns to the same point, and makes, in substance, the three following statements :—

(1) When the dielectric is a solid (a block of glass), and the distribution of electric force is not uniform, there are certain strains known to be produced (simple expansions, which are greatest at the place of shortest lines of force) ; and these known strains may account for the observed effects.

(2) There appears to be no electro-optic double refraction in the case of a uniformly charged Franklin's plate.

(3) But if one of the coatings be much reduced in size, or if we use, instead of it, a little mercury, contained within a small ring of glass, which is cemented to the upper surface of the plate at its centre, then the charging of the plate gives rise to a strain (a simple expansion, such as that produced by local rise of temperature) in the part of the plate immediately between the coatings, and a ray which passes through the plate and between the coatings is doubly refracted of course.

For some additional matter on the subject, not required here, I must refer to M. Wiedemann's treatise. The preceding statements give a correct view of a theory of the phenomena, which was advanced some years ago by M. Quincke ; the *first* statement giving his explanation of my experiment already referred to, and the *third* giving an explanatory account of a subsequent experiment of his own. My principal objection to this theory has always been, that it ignores

---

* *Die Lehre von der Electricität*, vol. ii. p. 125.

† All published subsequently to mine, and all, I believe, with explicit reference to it ; though Prof. Quincke's experiment was performed some ten years earlier.

those pure and intense effects which I obtained long ago in liquid dielectrics, particularly in carbon disulphide, and in a sensibly uniform field. The strains assumed in the *first* and *third* statements are undoubtedly real ; and it must be left to experiment to determine *whether*, and *how far*, they take effect in any actual case. With regard to my own early experiments on thick plates of glass, I am not aware of any evidence to show that these very small strains contributed to the observed effects in any degree whatever ; but I pass from these points to our proper subject.

The *second* of the preceding statements is not true in any other sense than as a record of several inadequate experiments. I find that a charged Franklin's plate, with uncoated margin so wide only as to give a small, working difference of potentials, acts upon transmitted light in the same way as olive oil, amyl oxide, or any other negative dielectric. My earlier experiments on the Franklin's plate need not be described, as they were chiefly of use in deciding between methods, and in showing the difficulties that had to be avoided or overcome. My last set of experiments on the subject were finished in July 1882 ; and the following account of them is drawn from full notes that were taken at the time.

One of my best plates was a rectangular piece of good English plate-glass, exactly $\frac{1}{8}$ of an inch thick, $2\frac{1}{2}$ inches wide, $4\frac{3}{8}$ long. This piece was one of a set, which were cut out of separate plates or fragments, and were then put together, and worked in block as one thick plate. The smaller ends of the thick plate were ground to sensibly parallel planes, and were polished carefully, till the glass gave a perfectly clear and undistorted view of neighbouring objects through the length of the block. Before going further with the preparation of the plates, I tested them separately in the polariscope; for I had found already that, unless the plates were tested and carefully selected, the experiments in view were almost hopeless.

Along with a couple of Nicol's prisms, two other pieces were employed—a rectangular slip of thin plate-glass used as a hand-compensator, and a larger slip used as a fixed compensator, the latter being placed in a simple screw-press, and subjected to horizontal tensions and compressions, which could be made to vary continuously through a considerable range. The two Nicols were placed in horizontal line with a good paraffin flame, and were exactly crossed, their principal sections being at 45° to the vertical. The plate was then fixed between the two Nicols, its faces vertical, and its terminal polished surfaces perpendicular to

the incident polarized pencil. The insertion of the plate restored the light always from extinction ; and the fainter this restoration, the more promising was the plate. The fixed compensator, which stood between the Nicols, and immediately after the plate, was then strained by trial, with or without small rotation of the second Nicol, till good extinction was obtained permanently ; and the feebler the strain thus required, and the purer and sharper the extinction obtained, the more promising was the plate. The hand-compensator was then inserted between the fixed compensator and the second Nicol, and supplied the last part of the test, which consisted in observing the degree of strain (horizontal tension or compression) which had to be applied, to give good restoration from extinction. When the requisite strain was small or very moderate, the plate was accepted as good, otherwise not.

The most of the plates that I have had in hand were pure failures under this test, and were therefore thrown aside as evidently quite unsuited for the electro-optic experiment. Of the set of *six* plates last started with, *four* were rejected without hesitation, the *fifth* was very imperfect, but worthy of trial, the *sixth* was good, though not perfect. Of another set of plates, which were only half as thick as the former, there was none even moderately good ; but one of them was retained, as in a small degree promising. The serious failure was generally in the last step of the test, that with the hand-compensator. When a good or very fair permanent extinction had been obtained by the joint action of the plate under trial and the fixed compensator, I found often that it required the exertion of almost all my strength on the hand-compensator, to get anything like a good restoration in the polariscope.

The light should have been well restored by a barely sensible effort ; but, in its passage through such a length of irregularly strained glass, it had lost ever so much of that sensitiveness under bi-refringent action which constitutes the whole value of the plane-polarized ray in any really delicate electro-optic work. No clear optical effect of moderate electric stress could be reasonably looked for in a plate such as that now mentioned, which allowed only a very small effect, or a mere trace of effect, to be given by a comparatively very strong bi-refringent action of the hand-compensator.

The plate chosen was coated with tinfoil in the usual way, the margin left on each face all round being rather less than a quarter inch. Projecting from the centre of each coating there was a small conducting tongue, made of a bit of tinfoil, which was folded several times on itself, opened out at one end, and pasted securely by that end to the coating. When

the paste had dried thoroughly, the plate was covered with a coat of thick lac-varnish all over, with exception of the polished ends and the conducting tongues. Another coat of the varnish was applied afterwards ; and the operation was repeated more than a dozen times, proper intervals of time being allowed for the drying of the varnish. When all was done, the tin coating was dimly visible in a good light, and the envelope of lac appeared to be perfectly continuous.

The plate was placed edgeways on the top of a fixed pillar of glass, and was attached to the pillar by a few drops of melted lac. Two perforated balls of brass, supported on separate pillars, were brought up to the plate at the centres of the two coatings; and the conducting tongues, passing into the perforations of the balls, were in good permanent contact with the brass. Through these balls the two coatings could be put into and out of connection with prime conductor and earth, and without any pressure on the plate. Two small screens of thin vulcanite were attached lightly to the plate on opposite sides of it, so as to protect the eye from all useless light.

Final State of the Best Plate.—The insulating power was not great. When one coating of the plate was connected with prime conductor and the other with earth, the spark-length between prime conductor and knuckle was at first about one sixth of an inch ; but afterwards, when the lac had hardened better on the plate, and in favourable weather, the spark-length was fully a quarter inch. Spark and shock were of course a good deal heavier than from the prime conductor unconnected.

The optical action of the best plate (still uncharged) was not sensibly different from what had been shown already in the process of testing. The sensibility of the ray under the action of the hand-compensator was indeed very satisfactory, considering that the light had passed through more than four inches of glass.

Method of Experiment.—In the simplest mode of working, the pieces were placed on the table in horizontal line and in this order :—paraffin flame, screen with narrow and short vertical slit, first Nicol with principal section at 45° to the vertical, the Franklin's plate with coated faces vertical, and terminal faces perpendicular to the incident pencil, fixed compensator, a little space for the hand-compensator, second Nicol at extinction. The axis of the small transmitted pencil of light was equidistant from the upper and lower edges of the coatings. In another arrangement, the collimator and lunette of a spectroscope were used, the lunette behind the second

Nicol, and the collimator (with very narrow vertical slit) before the first Nicol, the light employed being either a sunbeam or a beam from the bright sky. This arrangement served well in the case of the very thin plate already mentioned, which could not be managed well with the naked eye, because of the confusion produced by internal reflections ; but for the larger and better plates the first arrangement was preferred.

The electric force was applied most conveniently as follows. A Leyden jar stood on the table near the Franklin's plate ; and the outer coating of the jar and second coating of the plate were put permanently to earth. The jar was charged by twenty to thirty turns of the plate-machine : a common discharger, connected with the first coating of the Franklin's plate, was brought up to contact with the knob of the jar, but gradually, so as to avoid spark-discharge over the margin of the plate; and when the contact had been maintained for about three seconds, the connection was broken, and the plate was at the same time discharged. In this way the optical observation lasted only for the few seconds before and after discharge of the plate, so that small changes of intensity of the light in the polariscope were the more easily detected.

First Experiment.—Particular attention was given to the delicacy of action of the polariscope. The extinction was made as pure as possible by proper strain in the fixed compensator. The sharpness of the extinction was tested by the hand-compensator, the requisite delicacy being obtained when the light was restored clearly by feeble strains, horizontal compression and tension successively. When these conditions were fulfilled, the electric force, applied in the manner just described, gave good restoration from extinction in the polariscope, the light brightening gradually for a second or two, and then, after discharge of the plate, falling back to extinction at much the same rate. The intensity of the restored light was never great, being equal to that given by a very moderate compression in the hand-compensator. When the insulation was very defective, or the plate optically bad, the effect was very poor indeed, and could not always be seized with certainty; but when these unfavourable conditions were avoided, the rise and fall of the light, from extinction and back to it, were quite distinct and regular.

Second Experiment.—The light was restored faintly from extinction, as by *horizontal compression* of the fixed compensator. I say *as by* horizontal compression, because the action of the uncharged Franklin's plate in the polariscope was sometimes equivalent to horizontal compression, and had to be neutralized by horizontal tension of the fixed compensator ;

and then the desired effect was obtained by a small diminution of that horizontal tension. In any case, the permanent initial restoration required in this experiment, when tested by the hand-compensator, was clearly strengthened by a feeble horizontal compression, and clearly weakened by a feeble horizontal tension. When these conditions were fulfilled, the light was regularly and very clearly strengthened by charge of the plate, the intensity rising and falling gradually, —before and after discharge—as in the first experiment. Under adverse conditions, the insulation bad, or the plate optically imperfect, this experiment succeeded a good deal better than the first, the effect being, as it ought to be, distinctly stronger.

Third Experiment.—The light was restored faintly from extinction, as by *horizontal tension* of the fixed compensator ; and this initial effect was seen to be properly affected under the action of the hand-compensator, clearly weakened by a feeble horizontal compression, and clearly strengthened by a feeble horizontal tension. The electric force being applied as formerly, the changes now observed in the polariscope were contrary to those obtained in the second experiment, and apparently of equal range. During charge the light was weakened, its intensity falling regularly and very clearly for a second or two, and then, after discharge, returning to the initial value at much the same rate. In this experiment, as in the other two, the intensity of the effects was very moderate at the best ; but there was no uncertainty or indistinctness about the results, except when the conditions were known to be very unfavourable.

I have referred already to the earliest known instance of electro-optic double refraction. In that instance, the electric field lay between and around the ends of two straight collinear wires, at the centre of a block of glass, the thickness of glass between the terminals being (as in the present experiments) about $\frac{1}{8}$ of an inch, and the thickness traversed by the ray $\frac{3}{4}$ of an inch. It would be difficult to realize an electric field much more unlike that of the Franklin's plate ; and yet the optical effects obtained in that case were of precisely the same kind as those obtained in the present experiments,— negative double refractions with reference to line of electric force as axis. It appears thus, that *the fact of electro-optic double refraction in glass is not dependent on form of the electric field, or mode of distribution of the electric forces.*

There is one thing brought out by the preceding comparison which is at first sight not satisfactory. In the Franklin's plate as compared with the old dielectric, there was a con

siderable increase of thickness of the dielectric in the direction of the ray, and yet there was a large decrease of intensity of effect. But if we assume, as we may fairly do, that the quantity of optical effect varies as the square of the difference of potential of the two coatings, we see that a moderate increase of ray-length in the dielectric may be much more than counterbalanced by a moderate decrease of difference of potentials. Now in the old experiment and the new, the ratio of ray-lengths in the dielectrics was about 1 to 6, while the change of spark-length was from an average of 6 inches to a maximum of $\frac{1}{4}$ inch, implying a large fall of potential. I may even observe that the increase of ray-length in the present experiments appears to have told clearly on the intensity of the effect, because, in the old experiment, and in the most favourable circumstances, hardly any effect could be obtained with as little as an inch of spark-length.

But, further, we must remember those permanent and irregular strains which were sought to be eliminated in the preliminary testing of the plates. The disturbing influence of these strains may be expected to increase with every increase of ray-length in the dielectric, and with every decrease of the difference of potential. When the ray-length in glass amounts to several inches, I believe that it is not possible to get rid of this disturbance perfectly. In the best plates that I have worked with, not only was the disturbance present, but it always told seriously, weakening if not masking the effect of any very small birefringent action to which the transmitted ray could be subjected. Taking these things into account, and viewing the new phenomena and the old as cases of the same effect of electric force, I consider the small effects now obtained with the Franklin's plate to be as good as could fairly be expected, and better than could be expected confidently ; and I therefore hold it proved by experiment, that *electrostatically strained glass acts in the polariscope as if compressed along the lines of electric force, and thus always, whether the electric field is uniform or not.*

I conclude briefly with a simple and important argument, which appears to be secured now against all reasonable objection. With reference always to resultant effect in the polariscope, as characterized by (say) the hand compensator :— Electrically charged *glass* acts as if *compressed* along the lines of force ; electrically charged *resin* acts as if *extended* along the lines of force ; electrically charged *oil of colza*, a negative dielectric, acts precisely as glass *compressed* in a direction parallel to the lines of force ; electrically charged *carbon disulphide,* a positive dielectric, acts precisely as glass *extended* in a direc-

tion parallel to the lines of force ; and so forward uniformly (with variations of intensity and sign, and with occasional disturbance, mostly from known causes) through a list of more than 120 different dielectrics, as I have proved by experiments already published. The similarity of all these optical actions implies a similarity of condition in all the acting media. We infer that glass, resin, oil of colza, carbon disulphide, and all those other dielectrics, when *electrically charged*, are also *specially and similarly strained*. And it seems to be quite consistent with proper caution, in the absence of opposing evidence, to extend this conclusion to all dielectrics whatsoever.

We are led thus by the facts of electro-optics, and independently of all theory, to the conception and realization of *electrostatic strain*,—a strain maintained by the action of electric force, or (at least) in exclusive and indissoluble connection with that action, and sustained by the dielectric as an elastic medium,—a strain of one type in all dielectrics,—a strain essentially directional in liquids as in solids,—a strain *sui generis*. And in all this, or rather in the facts themselves, we have a remarkable confirmation of the theoretical views of Faraday and Maxwell.

Glasgow, 21st August, 1885.

Postscript.—In the charged Franklin's plate, the glass is compressed by the electric attraction of the two coatings; and it may be inquired how far this mechanical strain contributes to the effect obtained in the preceding experiments. I have had this question suggested to me by Sir William Thomson, as too important and too obvious to be neglected, and admitting also of a simple method of solution ; but I am sorry that the best answer obtainable with my present means is very vague and uncertain.

When the old Franklin's plate is laid flat, compressed by a weight uniformly distributed over it, and submitted to the old test in the polariscope, I find that it requires a total weight of $1\frac{1}{4}$ pound to give an effect equal to the old effect of electric charge. This compressing force of $1\frac{1}{4}$ pound must be much greater than the attraction of the electrically charged coatings, whose dimensions are about $2 \times 3\frac{1}{2}$ inches, their distance $\frac{1}{8}$ inch, and their difference of potentials at the moment of observation probably less than that corresponding to a spark of $\frac{1}{8}$ inch in air. It seems, therefore, that the part of the optical effect of electric charge which is due to compression of the glass must be very small, if not insensible. I should mention, however, that by a simple calculation, on the assumption

2 D 2

of an important determination made by Sir William Thomson[*],
the preceding figures give a superior limit of the attraction
of the coatings, which is as large as one *ninth* of the optically
equivalent compressing weight.   As to a definite solution of
the question, I hope to attempt that, or something equivalent,
very soon, in a set of experiments which I have had in view
for some time.

Glasgow, 26th August, 1885.

XLV. *Sequel to Paper on the Seat of the Electromotive Forces
    in a Voltaic Cell. Theories of* Wiedemann *and of* Helmholtz.
    By Professor OLIVER LODGE[†].

IN a recent *Beiblätter*[‡], Prof. G. Wiedemann points out that
in my summary of views and work in connection with
the seat of E.M.F. in the pile I have ignored his theory.   I
had in fact been mainly concerned with possible explanations
of the Volta-effect; while Prof. Wiedemann starts with this as
a datum, and on the strength of it explains the action of the
pile.   Moreover, since most of the theoretical opinions held on
this subject are summarized at the end of the second volume of
his *Elektricität*, while his own theory is given in the first volume,
along with the account of Volta-force experiments, I had over-
looked it.   To make amends for this oversight, for which I
beg to express my regret, and because I find it difficult to
summarize his opinions briefly, I trust I may be permitted
to give a rough semi-literal translation of his most conspicuous
passages as a help to other students of the subject.

Theory of G. Wiedemann, 1870. (Wied. *Elek.* i. p. 251 *et seq.*)

   "We have now to investigate in what way the electrical
forces in a closed circuit of two metals and a liquid (*e.g.* Zn, Cu,
dilute HCl) are excited.   We know that the constituents of
the binary compound contained in the liquid separate by the
passage of the current in such a way that the one (H) is set free
at the copper and an equivalent quantity of the other (Cl) at
the zinc, and that the latter combines with an equivalent
quantity of zinc to form ZnCl.   This process shows that the
deportment of the binary body between the metals consists no
longer only in a simple overbalancing attraction of its whole
mass for one or the other electricity, as in metals, but also in

---

[*] Reprint of Papers on Electrostatics (§ 340).
[†] Communicated by the Author, in continuation of paper in Phil. Mag.
for March, April, May, and June of the current year.
[‡] *Beiblätter zu den Annalen der Physik und Chemie*, 1885, No. 7,
Band ix. p. 533.

a special action of its constituents. Since the constituent Cl
is liberated where the + current enters the liquid, and H
where the negative enters, we suppose that each equivalent of
Cl in the compound HCl is charged with a definite quantity
of negative electricity, which conditions its attraction for the
opposite positive electricity. It is the *electro-negative element*
of the compound. So also must the equivalent H be charged
with + E and form the electro-positive element. These
charges could be produced by the combination of H and Cl
exactly in the same way as they are produced by the contact
of zinc and copper. Since the HCl formed is unelectrified,
we must suppose that atoms of the + and − constituents
contain equal quantities of + and −E.

" If now we immerse a Zn and a Cu plate into the dilute
HCl, we can conjecture that the zinc has a stronger attraction
for the electro-negative constituent (Cl) than for the H. In
consequence of this the molecule of HCl touching the zinc
will so lay itself that its electro-negative element is near the
zinc and its electro-positive element near the copper. At the
same time the molecules thus polarized act by electrical attrac-
tion on the constituents of the successive molecules of HCl,
arranging the whole row of molecules between the Zn and the
Cu plates as in the figure.

Zinc   Copper.

−   I   II   III   IV   +

Cl. H   Cl. H   Cl. H   Cl. H

+   (−)(+)   (−)(+)   (−)(+)   (−)(+)   −
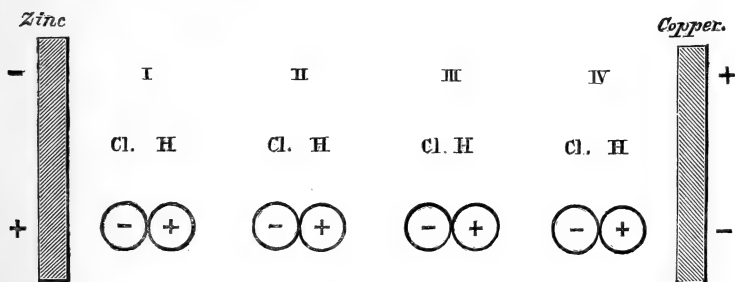
" By induction the negative electricity of the zinc-touching
electro-negative constituent, chlorine, would act on the E in
the zinc in such a way that the near parts will charge them-
selves positively, the further parts negatively. In the same
way the copper adjacent to the electro-positive element (H)
of the HCl atom lying against it will receive negative elec-
tricity. The positive will remove itself to the remoter regions.

" Thereupon the positive electricity in the zinc would com-
bine with the negative of the next-lying Cl atom, and this
latter with zinc to form unelectrical ZnCl. The electro-positive
atom H which was formerly joined to that Cl atom would itself
unite with the neighbouring atom of Cl belonging to the second

atom of HCl, at the same time combining with the electricity contained in this atom ; in the same way the hydrogen of the second atom—[the welcome letters *u. s. f.* are now not far ahead, and we will let them serve for the next fifteen or sixteen lines].

" It is evident that in this process there occurs a continual loss of *vis viva,* since the elements of the binary compound rushing up to the metal move with a definite velocity to the metal, and then are reduced to rest, either with formation of ZnCl or by being set free (H). This loss of *vis viva* is the equivalent of the heat which is evolved by the obviously occurring chemical process, which essentially is the solution of an equivalent of zinc in the acid. The same value must likewise be the work applied in effecting the redistribution of electricity.

" When, therefore, electricity begins to flow, work must be done, during the solution of Zn and liberation of an eq. of H from the liquid in the whole circuit, whether it be in the form of heat or of external work, which is equivalent to the heat-production attending that chemical process.

" The electrical shearing-force E is an accelerating force, so its work A in unit time is equal to its product with the quantity of electricity moved in unit time, m, and the distance s which the same travels, or

$$A = E . ms.$$

The product ms expresses the quantity of electricity which travels per second through the cross section of the conductor.

" If we have different combinations, as Zn, HCl, Cu ; or Mg, H_2SO_4 or NaCl,Cu ; or &c., we suppose that the same quantity of E travels per equivalent .... [a long appeal to the facts underlying Faraday's law is made to prove this] ; hence $ms =$ const.,

$$\therefore \ A = const. . E ;$$

or the E.M.F. is directly proportional to the heat generated by the decomposition of an equivalent of the binary compound and the solution of the zinc.

" For the production of steady currents, that electrical force can alone be active which depends on the unequal attraction and polarization of the atoms of the binary compound in the exciting liquid of the cell ; the electrical force at the contact-place of the metals which no mechanical changes can prelude must, on the other hand, be inactive. That this latter, if it perhaps opposed the metal liquid E.M.F. (as by immersion of zinc and lead in KCy solution), is not compensated by a definite part of the tension force, is proved by the afore-

said complete proportionality of the total electrical force (and E.M.F.) in the closed circuit with the said heat-equivalent of the chemical processes. It must then be neutralized in some other way. This would most simply happen on the hypothesis that, by contact of the exciting fluid with the metals, the E.M.F. is excited in a double way: first, by an unequally strong attraction of the masses of fluid and metal *as a whole* for the one or the other electricity; and, secondly, by the unequal attraction of the metals for the oppositely electrified components of the liquid. (This double pro-perty would be quite analogous to the following: a metal (*e. g.* zinc) can not only attract to itself by adhesion the whole mass of any given fluid (HCl), but also can exert a much stronger attraction for one constituent of the same (chlorine); just also as a magnet attracts iron, not only by reason of gravi-tation, but much more because of the magnetic polarization of its individual particles.)

"In consequence of the first unequal (mass) attraction for the electricities, the decomposable liquids would behave exactly according to the metallic law of tension, and in a closed circuit of metals and liquids a complete neutralization of electrical forces (and E.M.F.) would obtain; the second (chemical) action would, on the other hand, alone produce the electrical shearing-force effective in current formation and its accom-panying E.M.F.

"We will therefore in the sequel denote the total E.M.F. at the various junctions with strong letters, and that portion of the same of which no part engages in exciting the current by italics in brackets, and by italics without brackets the portion corresponding to the chemical work. In the closed circuit—zinc, sulphuric acid, copper—the whole active E.M.F. would then be

$$\mathbf{Cu/S} + \mathbf{S/Zn} + \mathbf{Zn/Cu} = Cu/S + S/Zn + (Cu/S) + (S/Zn) + (Zn/Cu).$$

"The experiments of Hankel and others give the total E.M.F. between the metal M and water, which we denote by $\mathbf{M/Aq}$, and which is compounded, according to the foregoing hypo-thesis, of the E.M.F. excited by the mass action of the water (M/Aq), and that excited by reason of its chemical polariza-tion M/Aq. If therefore we put into water a copper and a zinc plate, the total potential difference, or E.M.F. between its ends, is $\mathbf{Cu / Aq} + \mathbf{Aq / Zn}$. This is the quantity we should directly obtain if we connected the Cu and Zn immersed in water with the same named plate of a zinc-copper condenser, and after breaking the connection determined the charge of the condenser.

" On our hypothesis,

$$\mathbf{Cu/Aq} + \mathbf{Aq/Zn} = (Cu/Aq) + (Aq/Zn) + Cu/Aq + Aq/Zn.$$

If we close the circuit by connecting the zinc and copper plate by a copper wire, the force **Zn/Cu** adds itself to these E.M.F.s, and this force removes from the tension series of the metals the following forces, $(Cu/Aq) + (Aq/Zn)$; wherefore we get

$$\mathbf{Cu/Aq} + \mathbf{Aq/Zn} + \mathbf{Zn/Cu} = Cu/Aq + Aq/Zn.$$

But this last is the part of the total E.M.F. applied to the formation of the current. Hence *to the directly found contact-forces between different metals and water we must add the electromotive excitation of one metal on the other in order to get the current-forming E.M.F. in the circuit of a closed cell.*"

So far as I am able to see to the bottom of the foregoing theory its foundation appears to be as follows :—Contact experiments compel us to accept the summation law for the Volta-effects, or total differences of potential,

$$\mathbf{E} = \mathbf{Cu/Aq} + \mathbf{Aq/Zn} + \mathbf{Zn/Cu}.$$

The chemical theory constrains us to admit that the E.M.F. of a cell is the equivalent of the chemical action going on, and thus suggests that it equals the sum of some chemical contact forces ; or, in Wiedemann's notation, E ought also to equal

$$Cu/Aq + Aq/Zn.$$

How are these two requirements to be reconciled ?

Assume that at every junction there is a total force made up of two portions—a chemical force, such as Cu / Aq, and a physical force, which may be denoted by (Cu / Aq), and write the whole E.M.F. of a cell equal to the sum of all these chemical and physical junction-forces,

$$\mathbf{E} = Cu / Aq + (Cu / Aq) + Aq / Zn + (Aq / Zn) + (Zn / Cu).$$

We have then only to make the physical forces obey Volta's series law; so that

$$(Cu / Aq) + (Aq / Zn) + (Zn / Cu) = 0;$$

and we get the required relation

$$\mathbf{E} = Cu / Aq + Aq / Zn,$$

which harmonizes chemical and contact views.

Prof. Wiedemann's reconciliation of contact and chemical theories would thus seem to be somewhat of the same order as the later and less complete one of Fleeming Jenkin, quoted in my paper, § 6; but I cannot help feeling that the theory

of Prof. Wiedemann is rather fuller of hypothesis than most other contributions to the subject with which I am acquainted ; for it postulates

1. An unexplained difference of potential between metals in contact.
2. A similar difference of potential between the elements of a compound.
3. An unequal attraction of bodies for + and − E.
4. An unequal attraction of metals for chemical elements.
5. A chemical contact-force between metals and liquids, depending on No. 4, not obeying Volta's law.
6. A physical contact-force, depending on No. 3, obeying Volta's law.
7. Proportionality of the chemical contact-forces and the heats of combination.
8. A mechanical falling together of atoms accounting for heat-production at electrodes; and
9. That electrical actions go on between the molecules of a liquid, and between those molecules and metals immersed in it, according to the ordinary laws of electrostatics.

Not all of the above hypotheses, however, are to be regarded as independent : the dependence of Nos. 5 and 6 is stated, and it is possible that some of the others are intended to be likewise dependent, though I do not clearly see how.

In some of these hypotheses, for instance Nos. 4 and 5, and, with considerable differences, Nos. 6 and 7, Prof. Wiedemann's theory bears a resemblance to the views set forth by the present writer in the paper to which this communication is a sequel.

One obvious objection may be taken to the theory on a question of fact.   According to it, zinc half immersed in water is negative to copper half immersed in water (see diagram above) : but experiment has failed to exhibit anything of the kind ; and it is well known that Sir W. Thomson, Prof. Clifton, and others have shown that zinc and copper immersed in water or dilute acid are electroscopically at the same, or nearly the same, potential.

Theory of Von Helmholtz, 1847 *and later.*

There is another theory which I did not indeed ignore, but which I passed over with very insufficient mention, in the paper referred to (see footnote to § 9, Phil. Mag. April, p. 258); viz. the theory of Professor von Helmholtz, which he first stated in his great memoir of 1847, *Die Erhaltung der Kraft,* and

which he has improved and elaborated since (see Faraday Lecture of 1881).

This fascinating theory has a small hypothetical basis, viz. Nos. 3 and 9 of the above list; and on this foundation is erected an explanation of the Volta effect, a theory of electrolysis, and a great part of a theory of chemical combination.

Once grant, (1) that every substance has a specific attraction for positive or for negative electricity which can be exerted only through molecular distances, and (2) that the laws of electrostatics may be applied to the charges of atoms in a liquid; and the ease with which a multitude of phenomena are explained is surprising. I do not feel certain that a little too much is not explained; but we can postpone the consideration of possible objections until the theory itself is briefly stated.

Metals, and " electropositive " elements generally, attract positive electricity or positively electrified atoms whenever these come within range, *i. e.* within some molecular distance of the surface. Potassium and zinc attract strongly, copper and gold feebly. Oxygen, chlorine, and other " electronegative " elements, attract negative electricity in a similar manner.

Bring now two metals, say zinc and copper, into contact, and the superior attracting-power of zinc for positive electricity will at once charge it at the expense of the copper, so that the zinc touching-surface becomes strongly positive, and the copper surface strongly negative. Separate the metals, and they mostly discharge into each other; but a feeble charge remains if the surfaces in contact were large, and if they have been neatly separated; and this is the Volta effect.

Moreover since each metal has a definite attracting-power depending on itself only, Volta's series law is an obvious necessity.

If one of the substances had been an insulator much less loss need take place while separating them, and accordingly high charges are then found upon them even after separation (" frictional electricity ").

Now consider similarly two *atoms* in contact, forming, say, a water molecule. The hydrogen will be positively charged, the oxygen negatively. If some atoms should get knocked asunder they retain their charges and therefore tend to unite again, but, while separate, their mutual attractions and repulsions will preserve a uniformity of distribution throughout the liquid—*e. g.* the repulsion of similar charges will prevent a number of oxygen molecules crowding together; and if any cause should remove oxygen atoms from any part of the liquid, the vacancy will be instantly supplied by similar atoms repelled there.

The remarkable thing about the charges of atoms is, however, that they are all equal, and even for different atoms are still the same, or differ only according to simple multiples of some one absolute quantity; so that one atom may have three times as much negative electricity as hydrogen has positive, but not any fractional number. Such an atom may therefore combine with three of hydrogen atoms, and thus be called a triad. Another may be a dyad, &c. A given constant charge belongs to every unit of affinity which the atom possesses; and thus is the fact of chemical equivalence stated, though not accounted for. Faraday's law compels us to believe that atomic charges are thus multiples of one definite electric quantity, but why they should be so we are wholly unable to say. It looks as if electricity were atomic as well as matter; a sufficiently startling idea, as Helmholtz says.

Chemical affinity is thus due to the electrical attraction of oppositely charged atoms; not so much due to the attraction of the atoms themselves. This latter kind of attraction Helmholtz would not indeed deny, and he considers it may account for " molecular " modes of combination; but he regards it as much weaker than the electric forces, and as not effecting definite chemical combination.

We have ideas now concerning the size of atoms, and can calculate roughly what an atomic charge is. The charge of each atom is but small, but the aggregate charge of an appreciable number of them is enormous. It can be easily reckoned that if you take the opposite electricities out of a milligramme of water and give them to two spheres a mile apart, those two spheres will attract each other with a force of ten tons! Or, again, the electrical attraction of two atoms at any distance exceeds their gravitative attraction 71 thousand billion times. Upon such charges as these even very feeble external electrical influence may exert considerable force, and quite overpower any other kind of chemical affinity.

Plunge, therefore, two platinum plates into the liquid and keep them at some slightly different potential, say a volt or two : their surfaces are oppositely charged, and even this feeble charge may be sufficient to tear asunder the atoms of molecules which come close up to it*. If it is not sufficient, it

---

* It is easy to calculate the surface-density, and the difference of potential, on the above hypothesis, needed to tear asunder oppositely charged atoms attracting each other across molecular distance x. Let it be σ, and let the charge of an atom be q; then

$$2\pi\sigma q = \frac{q^2}{x^2}.$$

Moreover we know that 19,320 electromagnetic units can decompose 18 grammes of water, which allows $536 \times 3 \times 10^{10}$ electrostatic units of each

will at least hold a layer of oppositely charged atoms facing toward it across molecular distance ; so that near each plate we have an excessively thin condenser of enormous capacity ; but in the mass of the liquid is no such strain, the slightest E.M.F. being sufficient to redistribute the atoms here and to produce perfect equilibrium.   If the atoms are torn asunder by the electrode and liberated, fresh ones are continually supplied by the rest of the liquid, the state of strain being constantly re-formed and instantly broken down.

Thus are the phenomena of polarization and electrolysis explained.

Now insert into the liquid a pair of plates of zinc and copper in contact.   By the contact the zinc has become positive and the copper negative, and accordingly the zinc attracts the oxygen (or SO_4 radical) and combines with it : the copper attracts the hydrogen, and does the best it can with it.

This crudely is Helmholtz's view of a voltaic cell.

There is, however, one important detail not yet mentioned. I have spoken as if the work done by an electrode were to tear the atom from its combinations.   This is not exactly Helmholtz's view.   He adduces arguments to show that the work required to effect decomposition has for its object, not the separation of the atom from the liquid, but the separation of the atom *from its electric charge*.   It is to this that it clings, and this that has to be taken from it.   If it be made to give this up

---

kind of electricity per gramme ; so if n^3 be the number of molecules in a gramme of water, the charge of each dyad atom is

$$q = \frac{1 \cdot 6 \times 10^{13}}{n^3} ; \quad \doteq 1 \cdot 6 \times 10^{-11} \text{ probably.}$$

Hence

$$\sigma = \frac{1 \cdot 6 \times 10^{13}}{2\pi n^3 x^2} ; \quad \doteq 3 \times 10^{-12} \text{ probably ;}$$

and, the difference of potential between either plate and liquid being given by $4\pi x \sigma$, the whole difference of potential between the electrodes is

$$V = 8\pi x \sigma = 6 \cdot 4 \times \frac{10^{13}}{n^3 x} ; \quad \doteq \cdot 0064 \text{ electrostatic units probably,}$$

or 1·92 volt.

In reckoning the approximate numerical values above, I have assumed that $n = 10^8$ and that $nx = 1$.   The resulting decomposition force comes out, quite accidentally as far as I am concerned, very near that needed to decompose acid-water.   But I need hardly point out that *order of magnitude* is all that is really calculated in these figures ; and that not only decimals but even numerals, prefixed to the power of 10, have very little meaning.   The value of x may perhaps vary somewhat for different substances ; and as to the value of n, though that is definite enough, it is very probable that it ought to be something more like 2×10^8 than what I have above assumed it.

It is at any rate satisfactory that the electrostatic hypothesis should give, as a polarization E.M.F., a number so entirely comparable with actual results.

by a sufficient E.M.F., it is of small or no moment whether the ion be really set free, or be dissolved, or otherwise kept in the liquid.   But when the electrode is of such a metal that an ion can combine with it, that ion retains its charge, and accordingly very little E.M.F. is sufficient to decompose the liquid under such circumstances.

Without this statement it might be objected, that when a piece of zinc is plunged into acidulated water, since it has a strong attraction for positive electricity, it ought to attract the positively charged *hydrogen* atoms up to itself, instead of oxygen as commonly supposed.   I suppose Helmholtz would admit that it must do this to begin with, when isolated from other metals, on his theory, but that it has no way of separating and liberating atoms because it cannot get rid of their charges.   If it be kept at a sufficiently negative potential artificially it can indeed dispose of these charges, and it then does attract and liberate hydrogen.   But contact with copper raises it to a *positive* potential, and it then attracts negatively charged oxygen, rather than hydrogen, and combines with it ; while the negatively electrified copper seizes hydrogen atoms, tears their charges away from them, and sets them free.

I must confess, however, that I feel a difficulty here.   The natural tendency of zinc is, by hypothesis, to attract positive and repel negative atoms ; but, while a very feeble positive electrification applied to it is sufficient to reverse this tendency, a comparatively strong negative electrification is needed to enable it to exert that force which by the hypothesis is supposed to be *natural* to it.

In considering a Daniell cell, zinc / $ZnSO_4$ / $CuSO_4$ / copper, Helmholtz obtains the energy producing the current, by pointing out that electricity is removed from copper, which only attracts it feebly, and given to zinc which attracts it strongly. Zinc goes into solution and becomes positively charged, while an equivalent of equally positive copper comes out ; and since this results in a gain of energy, it follows that electricity must do more work in going to zinc, than in going to copper.

But if zinc attracts electricity so much more strongly than copper, why is it so easy to drive electricity across a copper / zinc junction ?   And why does no energy manifestation result at the junction from such an operation ?

The answer probably is, because of the large charge already existing at the junction ; the zinc has pulled as much positive electricity out of the copper as it wants, and there exists at the contact an electrical double layer, whose existence makes it quite easy for extraneous electricity to flow either way across the junction.

But, then, if zinc pulls so much electricity out of a piece of

copper with which it is put into contact, where does it all come from? And why does it not leave the copper *strongly* negative instead of only feebly so, as evidenced by Sir W. Thomson's electrified-needle form of experiment? Why, again, does this method of observing the Volta-effect, with the plates permanently in contact, agree so well with the old method of observing it by separation of the plates, if a great but uncertain part of the charge leak back as soon as separation beyond molecular distance is attempted?

These and similar difficulties occur to me in connection with this most interesting theory; and I state them, not with any idea that they are final and unanswerable, but because it is always serviceable to point out the apparent defects of a theory as well as its merits.

It will be seen that, whereas Helmholtz's theory starts with a hypothetical differential attraction of *matter for electricity*, and explains the chemical attraction of matter for matter on the strength of it, my view starts with a differential chemical attraction of *matter for matter* (*i. e.* zinc attracting oxygen more than copper attracts it), and on this basis works out the theory of the voltaic cell and of the Volta-effect.

In electrolysis proper both views may be at one, because here we are concerned with electrical attractions only; but Prof. Helmholtz's has the advantage, because it explains the fact of atomic charges, which mine has to assume. My view of electrolysis has hitherto been much less electrostatic than Prof. Helmholtz's, but also it has been much more vague. A great deal is to be said for the assumption of ordinary electrostatic attraction over molecular distances, and by adopting such more definite ideas I am in hopes of improving my theory further. And though, after all, none of these views can be really absolute, because they begin and end with action at a distance, still electrostatic attraction is a fact, and we know that it can be accounted for by a strain in a continuous medium. Hence phenomena reduced to electrostatics may be held to be provisionally "explained."

But beyond electrostatic attraction some other primary force is necessary; either *chemical affinity*, the attraction of atom for atom, or *electrical affinity*, so to speak, the attraction of atoms for electricity.

Chemical affinity is a fact, however it be accounted for; but, to enable it to explain everything, the fact of atomic charge must be permitted to likewise go without explanation. These are the necessary data for my view.

"*Electrical affinity*" is not known to be a fact; but if it be granted, everything is explained (barring a few outstanding difficulties), even the fact of atomic charge itself, though not

its numerical exactitude. This is the datum required for Helmholtz's theory.

It may thus be said that while the writer's view rests on two admitted facts which it does not attempt to explain, but, assuming them, explains other things from them; Helmholtz's theory rests on one unverified hypothesis, which, being granted, everything else follows; except indeed the numerical *equality* of atomic charges, which has to be regarded as experimentally demonstrated in both theories.

According to my view, the zinc of a cell pulls up the negatively charged oxygen atoms (or SO_4 radicals, whatever the real ions may be) to itself, not because they are electrified, but because they are oxygen. The electrical current produced is a secondary result caused by the chemical action.

According to Helmholtz, the zinc pulls the oxygen atoms because it is itself electrified by contact with copper, and because they are oppositely electrified by contact with hydrogen. The chemical action resulting is a secondary result caused by the electric forces.

Helmholtz's is thus a true " contact theory," and is in many respects like Sir W. Thomson's. Sir William postulates an attraction of zinc for copper, and from this explains the Volta-effect and the production of a current. I am unable to picture to myself exactly *how* the attraction of zinc for copper results in a difference of potential when they are put into contact; but undoubtedly such a force, if granted, would put a supply of energy at disposal which could account for the Volta-effect. And a difference of potential thus set up may result in an electrical decomposition of water and maintenance of current, just as in Helmholtz's theory.

I must confess that I am unable to feel quite comfortable about energy considerations with either of these theories of the voltaic cell; because it seems as if the metallic junction were, after all, driving the current, whatever be said about chemical energy. But in this I must certainly be wrong; that is to say, there must be some thorough way of reconciling these, by such men advocated, views with energy considerations, though I am unable satisfactorily to perceive it.

Both these contact-theories, in explaining the Volta-effect, ignore the existence of the oxidizing medium surrounding the metals. My view explains the whole effect as a result of this oxygen bath, and of the chemical strain by it set up. The other theory which likewise took account of the atmosphere is the old chemical one; but this leaves the aspect of the matter exceedingly vague. The strictures applied to it by Prof. Helmholtz (Faraday Lecture, 1881) are well deserved:—

" The so-called chemical theory of Volta's fundamental

experiment was rather indefinite; it scarcely did more than tell us—here is the possibility of a chemical process, here electricity can be produced. But which kind, how much, to what potential, remained indefinite. I have not found in all the papers which have been written for the defence of the chemical theory a clear explanation why zinc opposed to copper in liquids, where zinc really is oxidized and dissolved, becomes negative, and why in air and other gases it becomes positive, if the same cause (viz. oxidation) is at work."

To the chemical *strain* theory, held by me, none of this remark is in the least applicable. This theory *does not say* that zinc opposed to copper in a liquid is negative. It says that, changing the surrounding medium from air to acid-water, makes scarcely any difference ; and that accordingly connecting zinc and copper by a drop of water leaves them with the same respective potentials as they had before. The strain of oxygen-atoms towards a metal exists whether in air or water, but it can produce no effect in either case until at some point the oxygen be swept away by contact with another metal. Then instantly the chemical forces are able to do work, and to produce, if in air or other dielectric, the Volta-effect ; if in acid or other electrolyte, the voltaic current. The metallic contact equalizes the potential of the two metals in the one case; in the other it perpetually *fails* to equalize their potential. The equalization of an otherwise disturbed potential is its only effect.

And no indefiniteness exists as to either the kind or amount of the Volta-effect as so produced, for I have shown fully that *a* Volta-effect can be calculated in absolute measure for any pair of clean metals immersed in any medium, from purely thermo-chemical data ; but whether this effect is the real one or not is at present a matter of opinion.

These so-calculated effects undoubtedly agree in some cases with experimentally observed ones ; but whether they all so agree, and, if not, the extent to which they are erroneous, are matters mainly for future experiment to decide; and upon such agreement or disagreement between calculation and experiment my theory definitely stands or falls.

XLVI. *Intelligence and Miscellaneous Articles.*

ON A DIFFERENTIAL RESISTANCE THERMOMETER.
BY T. C. MENDENHALL.

THE determination or registration of the temperature at a distant or not easily accessible point is so extremely desirable that many methods for accomplishing this end have been proposed, and

to some extent made use of during the past fifty years.   Naturally enough electricity has been utilized in some way or other in the majority of these systems of telethermometry.

The requirements of the problem seem to be that the device or instrument used at the point, the temperature of which is to be ascertained, shall be of the greatest possible simplicity of construction, involving little or no motion in its parts, so that the liability to " get out of order " shall be reduced to the minimum ; and that at the observing or registering station, the necessary appliances 'shall possess a maximum of durability and simplicity—so that a minimum of time and skill will be demanded in making the observations.   The whole system must be certain in its indications and correct within a reasonable limit.

The first of these conditions is apparently sufficiently well satisfied by the thermo-electric-junction, which has probably been more extensively made use of than any other form of electric thermometer. It renders necessary, however, the use of a comparatively delicate galvanometer, and as the electromotive force of a single couple is small (it is difficult to use more than one in general practice) the results are subject to considerable errors arising from unknown or neglected sources of electromotive force.   This source of error becomes more important as the range of temperature measured becomes smaller, although it may be almost entirely avoided by care and skill on the part of the operator.   The well-known resistance method of Siemens satisfies the same condition very perfectly, and is certainly capable of giving good results when skilfully applied, at least throughout moderate ranges.

The desire to possess some form of electric thermometer which might be utilized in the study of certain problems connected with meteorology, especially the observation of soil and earth temperature, and the use of which would not demand greater skill than that of the ordinary meteorological observer, led to the device and construction of the instrument to be described, which may be called a " differential resistance thermometer."   It consists essentially of a mercurial thermometer, not unlike ordinary forms, except that the bulb is greatly enlarged so that the stem may have a diameter of something like a millimetre, and still leave the scale tolerably " open."   In one of the instruments already made 1° C. corresponds to about 5 millim. of the scale.   Running down through the stem is a fine platinum wire about ·08 millim. in diameter.   The lower end may be secured in the bulb so that it is kept straight in the bore of the stem, and at the lower end a heavier wire is sealed in the glass, so that metallic contact can be made with this wire both at the upper end and through the mercury at the lower.   It is evident that the resistance between these two points will depend largely (but not entirely) on the length of the platinum wire which is above the mercury in the tube, and this will depend on the temperature to which it is exposed.   When this temperature rises the resistance is decreased by an amount equal to the difference between that of the platinum wire which disappears and that of

the mercury which takes its place—less the increase in the resistance of the wire and mercury due to increase of temperature.

Let l=length of platinum wire exposed at 0°.
s=resistance per unit length (=length of 1°) of wire.
g=resistance per unit length (=length of 1°) of mercury.
k=temperature coefficient of platinum.
h=temperature coefficient of mercury.
R_0=total resistance at 0°.
R_t=resistance (including all) at t^o.

Then

$$R_t = R_0 - \{s(1-kl)-g\}t - (ks-gh)t^2. \quad . \quad . \quad . \quad (1)$$

This equation is not quite rigorous, but the approximation is very close. It is of the form

$$R_t = R_0 - Bt - Ct^2. \quad . \quad . \quad . \quad . \quad (2)$$

The simplest and best way of dealing with it is to determine the constants of the equation (2) by a series of observations making use of the method of least squares. From the result the resistance for any degree of temperature may be calculated, or, better, a curve can be constructed from which the temperature corresponding to any resistance can easily be read.

The advantage of this method over the use of a simple resistance coil is that the change in resistance accompanying a given change in temperature is much greater, and in fact it may be made as great as one desires. As a result the telephone may be substituted for the galvanometer in the resistance measurements, thus greatly simplifying the apparatus as well as increasing the rapidity with which observations may be made; or, if preferred, a much less sensitive galvanometer may be used. It also possesses the very great advantage of allowing an increase of delicacy as the range of temperature decreases. For earth temperatures this is very desirable, and it will easily be seen that thermometers of this kind can be constructed for a few degrees of range with which, by comparatively rude processes, the measurements may be correct within a very small fraction of a degree. For use in earth temperature measurements the thermometer will be enclosed in a strong brass tube for protection, and the connection with the point of observation made by means of a cable of heavy copper wire. The cable will of course form a part of R_0 in equation (2); but as it is a constant, the substitution of one cable for another, if necessary, will affect the position and not the form of the calibration curve. Its resistance must be small, relatively, and the influence of temperature upon it may be neglected.

With this device a temperature observation may be taken in less than a minute, no time being consumed in the preparation of liquids of known temperature at the observing station, as in the use of the thermo-junction or the resistance coil.—Silliman's *American Journal,* August 1885.

ON THE DETERMINATION OF THE COEFFICIENTS OF INTERNAL
FRICTION. BY WALTER KÖNIG.

The author determined the coefficients of a number of liquids by
the method of vibrating disks, and also by that of flow from capillary
tubes, and obtained numbers which agree with those obtained by
other inquirers.

He also examined whether electrification and exposure in a
magnetic field had any influence on this coefficient, and obtained a
negative result.—Wiedemann's *Annalen*, No. 8, 1885.

NOTE ON THE TRANSMISSION OF LIGHT BY WIRE-GAUZE
SCREENS. BY S. P. LANGLEY.

In the beginning of the present year a friend sent me a series of
wire-gauze screens, which he used to diminish the apparent bright-
ness of stars in making meridian observations, with a request that
I would determine photometrically the amount of light transmitted
by them. As such screens are occasionally employed in astronomical
work, particularly in the use of the heliometer, I have thought the fol-
lowing account of our experience of sufficient interest to make public.

I used for the measurements a photometer-box originally con-
structed for another purpose, and an opaque wheel or disk having
radial slits of variable width, which, placed in the path of a ray of
light and rotated with sufficient velocity, can be made to reduce the
light to any desired fraction of its original intensity. (This I have
employed for some years for photometric measurements when it is
desirable to avoid the use of polarizing-apparatus.) In the centre
of the photometer-box was a sliding Bunsen disk, which could be
viewed from above by a suitable arrangement of mirrors. The
open ends of the box were directed to two opposite windows, and the
disk placed in such a position that its sides were equally illuminated.
The wire screen was then placed over one end of the box, the wheel-
photometer in front of the other end, and the apertures of the
latter altered until the equality of illumination of the Bunsen disk
was restored. The screen then cut off the same amount of light as
the wheel. From several series of measurements made in this way,
it was found that

1 screen transmitted .... ·395 + ·004 of the incident light.
2 screens superposed transmitted ·144 ∓ ·004   ,,   ,,
3   ,,   ,,   ,,   ·052 + ·003   ,,   ,,

These numbers, as was to be expected, are nearly in geometrical
progression. The screens were returned to the sender and the
results communicated to him; but he wrote that, upon trial, he
found the reduction of light very much greater than the above
values, three superposed screens reducing the light of a star by 7·1
magnitudes, which corresponds to a transmission of only ·0014.

I was at that time absent, and my assistant, Mr. J. E. Keeler,
undertook the investigation of the cause of the discrepancy, which
he attributed to loss of light by diffraction under the circumstances
in which the screens were used by their owner, *i. e.* in front of the
object-glass of a telescope directed upon a star. With diffuse

light, such as was used in the measurements with the photometer-box, no loss due to this cause was possible.

In the apparatus devised by Mr. Keeler for an experimental determination of the loss by diffraction, the star was replaced by an illuminated pinhole in the focus of a 3-inch collimating-telescope. This was viewed by an observing-telescope of nearly equal size, in the eye-tube of which was an unsilvered plane-glass mirror, which reflected into the eye-piece a comparison star—the image of an illuminated pinhole produced by a collimating-telescope at right angles to the other two. In the path of the rays from this tele-scope could be interposed the wheel-photometer. The light before entering the first pinhole suffered reflection from an unsilvered glass surface, in order to reduce its intensity to that of the com-parison star.

The two images in the field of view having been adjusted to equality, the wire-gauze screen was interposed between the object-glasses of the collimating- and observing-telescopes, reducing the light of the star and producing around it the well-known diffraction-image of a network. The wheel-photometer was then introduced, and the intensity of the comparison star reduced until it was equal to the central image of the other. By enlarging the pinholes until the superposition of the colours produced white light, the intensity of the diffraction-images could also be estimated.

It was thus found that the central image had only ·175 of its original brightness, which would therefore be the proportion trans-mitted by the screen under these conditions, and that the brightness of each of the four first spectra was ·05 of that originally possessed by the central image. Two thicknesses of the wire-gauze transmitted barely ·02, as measured by the intensity of the central image.

The screens with which these experiments were made were much coarser than the original ones, and it was expected that the effect of diffraction would be less pronounced. The transmission of one thickness, measured by the photometer-box, was ·47; of two thicknesses. ·21.

Finally, the apertures of the screen and the diameter of the wire were measured by a micrometer-microscope and the apertures found to occupy ·465 of the total area of the screen.

It was concluded, therefore, as the result of the experiments :—

1. That the transmission, as measured by the photometer-box, was equal to the ratio of the sum of the areas of the apertures of the screen to its total area, and therefore could be considered to be the true transmission of the screen ; and

2. That the much smaller transmission of the screen, when used in front of the object-glass of a telescope to diminish the apparent brightness of a star, is satisfactorily accounted for by the loss of light caused by diffraction under these circumstances.

3. That screens used for this purpose should have their constants determined by special experiments of the nature of those just de-tailed, and that their photometric use should then be limited to the reduction of the light of bodies possessing a small angular magnitude.
—Silliman's *American Journal*, September 1885.

THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

———◆———

[FIFTH SERIES.]

NOVEMBER 1885.

XLVII. *The Luminiferous Æther.* By DE VOLSON WOOD,
C.E., M.A., *Professor of Mechanical Engineering in Stevens
Institute of Technology, Hoboken, N.J.*[*]

TWO properties of the luminiferous æther appear to be
known and measurable with a high degree of accuracy.
One is its ability to transmit light at the rate of 186,300 miles
per second[†], and the other its ability to transmit from the
sun to the earth a definite amount of heat-energy.

In regard to the latter, Herschel found, from a series of
experiments, that the direct heat of the sun, received on a
body at the earth capable of absorbing and retaining it, is
competent to melt an inch in thickness of ice every two hours
and thirteen minutes[‡]. This is equivalent to nearly 71 foot-
pounds of energy per second.

In 1838 M. Pouillet found that the heat-energy transmitted
from the sun to the earth would, if none were absorbed by
our atmosphere, raise 1·76 gramme of water 1° C. in one
minute on each square centimetre of the earth normally
exposed to the rays of the sun[§].

This is equivalent to 83·5 foot-pounds of energy per second,

[*] Communicated by the Author.
[†] Professor Michelson found the velocity of light to be 289,740 metres
per second in air, and 299,828 metres in a vacuum, giving an index of
refraction of 1,000,265. Journ. of Arts and Science, 1879, vol. xviii.
p. 390.
[‡] 'Familiar Lectures on Scientific Subjects,' by Sir John Herschel,
p. 65.
[§] *Comptes Rendus,* 1838, tom. vii. pp. 24–26.

and is the value used by Sir William Thomson in determining the probable density of the æther*.   Later determinations of the value of the solar constant by MM. Soret, Crova, and Violle have made it as high as 2·2 to 2·5 calories.   But the most recent, as well as the most reliable, determination is by Professor S. P. Langley, who brought to his service the most refined apparatus yet used for this purpose, and secured his data under favourable conditions; from which the value is found to be 2·8 ± calories† with some uncertainty still remaining in regard to the first figure of the decimal.   We will consider it as exactly 2·8 in this analysis, according to which, there being 7000 grains in a pound and 15·432 grains in a gramme, we have for the equivalent energy

$$\frac{2\cdot8 \times 15\cdot432}{7000} \times \frac{9}{5} \times \frac{772 \times 144}{0\cdot155 \times 60} = 133 \text{ foot-pounds}$$

per second for each square foot of surface normally exposed to the sun's rays, which value we will use.   Beyond these facts, no progress can be made without an assumption.   Computations have been made of the density, and also of the elasticity, of the æther founded on the most arbitrary, and in some cases the most extravagant, hypotheses.   Thus, Herschel estimated the stress (elasticity) to exceed

$17 \times 10^9 = (17,000,000,000)$ pounds per square inch‡;

and this high authority has doubtless caused it to be widely accepted as approximately correct.   But his analysis was founded upon the *assumption* that the density of the æther was the same as that of air at sea-level, which is not only arbitrary, but so contrary to what we should expect from its non-resisting qualities, as to leave his conclusion of no value.   That author also erred in assuming that the tensions of gases were as the wave-velocities in each, instead of the mean square of the velocity of the molecules of a self-agitated gas; but this is unimportant, as it happens to be a matter of quality rather than of quantity.   Herschel adds, "Considered according to any hypothesis, it is impossible to escape the conclusion that the æther is under great stress."   We hope to show that this conclusion is not warranted ; that a great stress necessitates a great density; but that both may be exceedingly small.   A great density of the æther not only presents great physical difficulties, but, as we hope to show,

* Trans. Roy. Soc. Edinburgh, vol. xxi. part 1.
† Am. Journ. of Arts and Science, March 1883, p. 195.   Also *Comptes Rendus.*
‡ 'Familiar Lectures,' p. 282.

is inconsistent with the uniform elasticity and density of the æther which it is believed to possess; and every consideration would lead one to accept the lowest density consistent with those qualities which would enable it to perform functions producing known results.

In a work on the ' Physics of Æther,' by S. Tolver Preston, it is estimated that the probable inferior limit of the tension of the æther is 500 tons per square inch, a very small value compared with that of Herschel's. But the hypothesis upon which this author founded his analysis was—The tension of the æther exceeds the force necessary to separate the atoms of oxygen and hydrogen in a molecule of water; as if the atoms were forced together by the pressure of the æther, as two Magdeburg hemispheres are forced together by the external air when there is a vacuum between them. This assumption is also gratuitous, and is rejected for want of a rational foundation.

Young remarks:—"The luminiferous æther pervading all space is not only highly elastic, but absolutely solid."[*] We are not certain in what sense this author considered it as solid ; but if it be in the sense that the particles retain their relative positions, and do not perform excursions as they do in liquids, it is a mere hypothesis, which may or may not have a real existence. If it be in the sense that the particles suffer less resistance to a transverse than to a longitudinal movement, there are some grounds for the statement, as shown in circularly-polarized light. Bars of solids are more easily twisted than elongated, and generally the shearing-resistance is less than for a direct stress. It certainly cannot be claimed that the compressibility of the æther (in case we could capture a quantity of it) is less than that of solids.

Sir William Thomson, in making a probable estimate of the density of the æther, made a more plausible hypothesis, by assuming that "the maximum displacement of the molecules of the æther in the transmission of heat-energy was $\frac{1}{50}$ of a wave-length of light, the average of which may be taken as $\frac{1}{50,000}$ of an inch." Hence the displacement was assumed to be $\frac{1}{2,500,000}$ of an inch; by means of which he found the weight of a cubic foot to be $\frac{2}{3} \times 10^{-20}$ of a pound[†]. We also notice that one Belli estimated the density of the æther to be $\frac{1}{2} \times 10^{-13}$ of a pound[‡]; but M. Herwitz, assuming this value to be too small and Thomson's as too large, arbitrarily assumed it as

* Young's Works, vol. i. p. 415.
† Phil. Mag. 1855 [4] ix. p. 39.
‡ Cf. *Fortschritte der Physik*, 1859.

10^{-18} of a pound per cubic foot; but arbitrary values are of small account unless checked by actual results.

We propose to treat the æther as if it conformed to the Kinetic Theory of Gases, and determine its several properties on the conditions that it shall transmit a wave with the velocity of 186,300 miles per second, and also transmit 133 foot-pounds of energy per second per square foot. This is equivalent to considering it as gaseous in its nature, and at once compels us to consider it as molecular; and, indeed, it is difficult to conceive of a medium transmitting light and energy without being molecular. The Electromagnetic Theory of Light suggested by Maxwell, as well as the views of Newton, Thomson, Herschel, Preston, and others, are all in keeping with the molecular hypothesis. If the properties which we find by this analysis are not those of the æther, we shall at least have determined the properties of a substance which might be substituted for the æther, and secure the two results already named. It may be asked, Can the Kinetic theory, which is applicable to gases in which waves are propagated by a to-and-fro motion of the particles, be applicable to a medium in which the particles have a transverse movement, whether rectilinear, circular, elliptical, or irregular? In favour of such an application, it may be stated that the general formulæ of analysis by which wave-motion in general, and refraction, reflection, and polarization in particular, are discussed, are fundamentally the same; and in the establishment of the equations the only hypothesis in regard to the path of a particle is—It will move along the path of least resistance. The expression $V^2 \propto e \div \delta$ is generally true for all elastic media, regardless of the path of the individual molecules. Indeed, granting the molecular constitution of the æther, is it not probable that the Kinetic theory applies more rigidly to the æther than to the most perfect of the known gases?[*]

The 133 foot-pounds of energy per second is the solar-heat energy in a prism whose base is 1 square foot and altitude 186,300 miles, the distance passed over by a ray in one second; hence the energy in 1 cubic foot will be

$$\frac{133}{186,300 \times 5280} = \frac{4}{3 \times 10^7} \text{ foot-pounds.} \quad . \quad . \quad (1)$$

Where results are given in tenth-units of high order, as in the last expression, it seems an unnecessary refinement to

---

[*] See also remarks by G. J. Stoney, Phil. Mag. 1868 [4] xxxvi. pp. 132, 133.

retain more than two or three figures to the left hand of the *tens*; and we will write such expressions as if they were the exact results of the computations.

If V be the velocity of a wave in an elastic medium whose coefficient of elasticity, or, in other words, its tension, is e and density δ, both for the same unit, we have the well-known relation

$$V = \sqrt{\frac{de}{d\delta}}.$$

And for gases we have

$$e = \delta^\gamma,$$

where $\gamma = 1\cdot4$; and the differential of the latter substituted in the former gives

$$V = \sqrt{\frac{\gamma e}{\delta}}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

The tension of a gas varies directly as the kinetic energy of its molecules per unit of volume. If v^2 be the mean square of the molecules of a self-agitated gas, we have

$$e \propto \delta v^2, \text{ or } v^2 = x\frac{e}{\delta}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

where x is a factor to be determined. Equations (2) and (3) give

$$v^2 = \frac{x}{\gamma} V^2. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

Assuming, with Clausius, that the heat-energy of a molecule due to the action of its constituent atoms, whether of rotation or otherwise, is a multiple of its energy of translation, we have for the energy in a unit of volume producing heat,

$$\tfrac{1}{2}y\delta v^2,$$

where y is a factor to be determined. If c be the specific heat of a gas, w its weight per cubic foot at the place where $g = 32\cdot2$, J Joule's mechanical equivalent, τ its absolute temperature; then the essential energy of a cubic foot of the medium will be $cw\tau$J; and observing that $w = g\delta$, we have

$$\tfrac{1}{2}y\delta v^2 = cg\delta\tau\text{J}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (5)$$

which, reduced by (4), gives

$$xy = \frac{2cg\gamma\tau\text{J}}{V^2}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (6)$$

the second member of which is constant for a given gas. To

find its value, we have

	Hydrogen.	Air.	Oxygen.
Specific heat*	3·4093	0·2375	0·2175
Velocity of sound, feet per second at $\tau = 493°·2$. }	4163	1090	1040

and $g = 32·2$, $\gamma = 1·4$, $J = 772$. These, substituted in the second member of (6), give

xy for hydrogen . . . . 6·599
  „ air . . . . . . 6·706
  „ oxygen . . . . . 6·596
                        3)19·901
          Mean . . . . 6·63

This value, which is nearly constant for the more perfect gases, we propose to call *the modulus of the gas*, and represent it by μ; and for the purposes of this paper we will use

$$\mu = 6·6.$$

This relation of the product xy being a constant, has, so far as we are informed, been overlooked by physicists, and is worthy of special notice, since it determines the value of one of the factors when the other has been found. Krönig, Clausius[†], and Maxwell give for x the constant number 3, but variable values for y [‡].

We are confident that the value of x is not strictly constant; or if it is, it exceeds 3, since the effect of the viscosity of a gas would necessitate a larger velocity to produce a given tension than if it were perfectly free from internal friction. For our purpose it will be unnecessary to find the separate values of x and y; but if we have occasion to use the former in making general illustrations, we will call it 3, as others have done heretofore. If the correct value of x exceeds 3, it will follow that the velocity of the molecules exceeds the values heretofore computed[§]. According to Thomson, Stokes showed that in the case of circularly polarized light the energy was

---

* Stewart on 'Heat,' p. 229.
† Phil. Mag. 1857 [4] xiv. p. 123.
‡ 'Theory of Heat,' pp. 314 and 317. Maxwell states that the value for y is probably equal to 1·634 for air and several of the perfect gases. This would make $x = 4$ nearly.
§ Maxwell gives for the mean square of the velocities (or, in other words, the velocity whose square is the mean of the squares of the actual velocities) of the molecules, in feet per second at 493°·2 F. above absolute zero, hydrogen 6232, oxygen 1572, carbonic oxide 1672, carbonic acid 1570. Phil. Mag. 1873, p. 68. Our equation (4) gives for air 1593.

the limit of the capacity of the pumps ; and Professor Rood produced one of $\frac{1}{390,000,000}$ of an atmosphere[*] without passing the limit of action of his apparatus. The latter gives a pressure per square foot of $\frac{14 \cdot 7 \times 144}{390,000,000} = \frac{1}{180,000}$ of a pound. This, in round numbers, is 140 times the value given in equation (11). Even at this great rarity of the atmosphere, the quantity of matter in a cubic foot of the air would be some 200 million million times the quantity in a cubic foot of the æther—such is the exceeding levity of the æther.

Admitting that the æther is subject to attraction according to the Newtonian law, and of compression according to the law of Mariotte, we propose to find *the relation between the density of the æther at the surface of an attracting sphere and that at any other point in space,* providing that the sphere be cold and the only attracting body, and the gas considered the only one involved.

Let δ_0, e_0, w_0 be respectively the density, elasticity, and weight of a unit of the medium, whether æther, air, or any other gas, at the surface of the sphere; δ, e, w, the corresponding quantities at a distance z from the surface of the sphere; r the radius of the sphere, g_0 the acceleration due to gravity at its surface, and g that at distance $r + z$ from the centre of the sphere. Then

$$\frac{\delta}{\delta_0} = \frac{e}{e_0} = \frac{w}{g} \div \frac{w_0}{g_0}$$

and

$$g = g_0 \frac{r^2}{(r+z)^2} ;$$

$$\therefore \quad e = \frac{e_0}{w_0} \cdot \frac{g_0}{g} w = \frac{e_0}{w_0} \frac{(r+z)^2}{r^2} w. \quad . \quad . \quad . \quad (12)$$

But

$$de = -w\,dz = -g\delta\,dz ; \quad . \quad . \quad . \quad . \quad (13)$$

$$\therefore \quad \frac{de}{e} = -\frac{g_0 \delta_0}{e_0} \cdot \frac{r^2}{(r+z)^2} dz.$$

Integrating between e and e_0, $r + z$ and r, we have

$$e = e_0 \epsilon^{-\frac{g_0 \delta_0}{e_0} \cdot \frac{rz}{r+z}}, \quad . \quad . \quad . \quad . \quad (14)$$

$$\delta = \delta_0 \epsilon^{-\frac{g_0 \delta_0}{e_0} \cdot \frac{rz}{r+z}}. \quad . \quad . \quad . \quad . \quad (15)$$

Neglecting the attraction of the earth for the æther, and

considering the sun as the only attracting body, we have g_0 at the sun $28 \cdot 6 \times 32 \cdot 2$, and at the earth $z = 210\, r$, $r = 441,000$ miles, the sun's radius; $\delta = \frac{2}{35} \times 10^{-24}$, equation (9), and $e = \frac{4}{33} \times 10^{-6}$; and these, in (14) and (15), give

$$e = e_0 \epsilon^{\dfrac{28 \cdot 6 \times 32 \cdot 2 \times 2 \times 33 \times 10^6}{4 \times 35 \times 10^{24}} \times \frac{210}{211} \times 441,000 \times 5280}$$

$$= e_0 \epsilon^{\frac{1}{1,000,000}} \text{ nearly,} \quad \ldots \quad \ldots \quad (16)$$

and

$$\delta = \delta_0 \epsilon^{\frac{1}{1,000,000}} \text{ nearly,} \quad \ldots \quad \ldots \quad (16')$$

for the tension and density of the æther at the surface of the sun under the conditions imposed. But the millionth root of ϵ is practically unity; hence the elasticity and density at the sun is practically the same as at the earth.

Now, starting at the sun with this result, and finding the density at a distance z from it, then making z infinite, we shall get the 995,000th root of ϵ, the value of which is also sensibly equal to unity; hence the density at infinity would be sensibly the same as at the surface of the sun, the difference in the densities at the sun and at infinity being less than $\frac{1}{1,000,000}$ part of that at the sun. In order to make the density vary sensibly with the distance, the attraction of the central body must be something like a million times as great as that of the sun, or have a diameter a million times as large; but there being no such known body, therefore *the density and tension of the æther may be considered uniform throughout space.* Such has been our conception of it; and it is an agreeable surprise to find it so fully confirmed by analysis.

If the density were uniform, the weight of a given volume of it would vary as the force of gravity. At the surface of the sun a cubic foot would weigh [equation (10) multiplied by $28 \cdot 6$, or] 57×10^{-24}; hence, for a height h it would weigh

$$\frac{57}{10^{24}} \int_0^h \frac{r^2}{(r+z)^2}\, dz = \frac{57}{10^{24}} \cdot \frac{rh}{r+h}, \quad \ldots \quad \ldots \quad (17)$$

which for $h = \infty$ becomes $\frac{13}{10^{14}}$ of a pound, which is the pressure upon a square foot of the sun of a column of infinite height under the conditions imposed. This would compress the first foot of the column about $\frac{1}{1,000,000}$ of its length, and would cause a corresponding increase in the density, the value of which, after this compression, will be found by multiplying the value given in equation (9) by $\frac{999999}{1,000,000}$, which will leave the result sensibly the same as before. Hence, from this standpoint, we

again conclude that the density of the æther may be considered as sensibly uniform throughout space, providing its temperature be essentially uniform.

If we assume that the law of the resistance by which the æther opposes the motion of a body varies as the square of the velocity of the body, we are still unable to assign the coefficient which will give the numerical value ; but it is safe to assume that the entire mass of the æther occupying the path of a body moving through it, will not have a velocity imparted to it exceeding that of the body ; but to be on the safe side, we will assume that it imparts a velocity equal to itself. The energy thus imparted will be lost to the body. To simplify the case, consider a planet moving in a circular orbit : r the radius of the planet, d its distance from the sun, D its specific gravity compared with water as unity, v_1 the velocity in its orbit ; then the mass of æther occupying the place of the planet during one revolution about the sun will be, using equation (9),

$$\frac{2}{35 \times 10^{24}} \pi r^2 \times 2\pi d,$$

which, multiplied by $\frac{1}{2}v_1^2$, will give the energy imparted to it. The kinetic energy of a planet, neglecting its rotation, will be

$$\frac{4}{3}\pi r^3 \times 62\frac{1}{2} D \times \frac{v_1^2}{2g}.$$

Dividing the former, after multiplying it by $\frac{1}{2}v_1^2$, by the latter gives

$$\frac{1}{7 \times 10^{24}} \cdot \frac{d}{r\mathrm{D}} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (18)$$

for the fraction of the energy lost during one revolution about the sun. Applying this to the earth, we have

$$d \div r\mathrm{D} = 93{,}000{,}000 \div 3912 \times 5\frac{1}{2} = 43000,$$

and (18) becomes

$$\frac{6}{10^{22}} \text{ nearly,} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (19)$$

for the fraction of the energy lost in one year; and hence *at this rate* would require more than 1,666,000 trillion (1,666,000,000,000,000,000,000) years to bring it to rest.

Equation (18) is not applicable to the resistance offered to a comet, on account of the elongated orbit of the latter ; but some idea of the effect of the resistance of the æther to the movement of a comet may be found by considering what

it would be if the orbit were circular, having for its radius the perihelion distance. According to Professor Morrison, the perihelion distance of the great comet (6), 1882[*], was 716,200 miles, its aphelion distance will be 5,000,000,000 miles, the diameter of its nucleus shortly before disappearing on the solar disc was 7600 miles, the velocity at perihelion 295 miles per second and at aphelion 75 feet per second. But little is known in regard to the density of comets ; but to be on the safe side we will assume it as $\frac{1}{1000}$ that of water. This data will reduce (18) to 13×10^{-18} for the fraction of energy lost during one of its revolutions about the sun ; and as it would make a revolution in, say, 20 hours, it would lose in one of our years about 57×10^{-16} of its energy, *at which rate* it would go on for 170 trillions of years. Similarly, at its aphelion its *rate* of loss would be less than $\frac{1}{6} \times 10^{-15}$ of its energy in more than 2000 years—the time of one revolution in its orbit.

The most careful observations and calculations have failed to detect any effect due to the resistance of matter in space ; and the above analysis shows that, within historic times, it has in any case scarcely amounted to an infinitesimal, certainly not sufficient to be measured. And when we consider that our assumptions have been very largely on the unfavourable side, and, further, that the energy imparted to the æther may, partly at least, be restored to the body, we assume that its resistance never can be measured. Laplace, when he found that the force of gravitation, if propagated by an elastic medium, must have a velocity exceeding 100 million times that of light, concluded that astronomers might continue to consider its action as instantaneous (*Mécanique Céleste*, B. x. ch. viii. p. 22, 9035) ; so may we, with as much confidence, continue to consider the resistance of the æther as *nil*.

Equation (6) gives

$$c\tau = \frac{6 \cdot 6 (186300 \times 5280)^2}{2 \times 32 \cdot 2 \times 1 \cdot 4 \times 772} = 92 \times 10^{12}, \quad . \quad . \quad (20)$$

from which the specific heat of the æther may be found if its temperature were known. M. Fourier, the first to assign a value to *the temperature of space*, assumed it to be somewhat inferior to the temperature at the poles of the earth, or about 50° C. to 60° C. below zero[†]. M. Pouillet, considering the

* ' Monthly Notices of the Royal Astronomical Society,' vol. xliv. 2, p. 54.
† *Ann. der Chemie*, tome xvii. p. 155.

atmosphere as a diathermanous medium, capable of absorbing in different degrees the radiant heat from the sun and the dark heat from the earth, deduced for the heat of space—or, as he and Fourier called it, the stellar heat—approximately -142° C.[*] (-287° F.), which is about 174° F. above absolute zero. It is well known that Pouillet's data were imperfect, several important elements being neglected, notably that of the humidity of the air ; still it is not only the first, but, so far as we know, the only attempt to formulate this relation. It served to show, what has since been indicated by more direct experiments, that the temperature of space is very low. The delicate experiments of Professor Langley, before referred to, show a great difference in the degree of absorption by our atmosphere of different wave-lengths. The mean of the values for nine different wave-lengths, treated by M. Pouillet's formula, gives 139° F. above absolute zero, and the smallest value of absorption, which was for the infra-red, gives only 71° F. above absolute zero for the heat of space.

The heat of space may be considered as composed of three parts:—(1) stellar heat, (2) the heat contained in the dark matter of space, (3) the essential heat of the æther.

1. By the stellar heat we mean the heat received directly from the stars. It is a matter of easy calculation that, if the 50,000,000 of stars supposed to be visible with the most powerful telescopes were all at the distance of the nearest fixed star (a Centauri), or 221,000 astronomical units from the earth, and if each radiated the same amount of heat as our sun, the intensity varying as the inverse squares of the distances, the earth would receive from them all less than $\frac{1}{1000}$ as much heat as it now receives from the sun. And when we consider that only a very few stars are within measurable distances, and that the remote ones may be, when compared with these, well-nigh infinitely distant, it is evident that the amount of heat received from the stars is insignificant and may be discarded at the earth.

2. It is certain that there is a large amount of dark matter in space, since the meteoric dust and meteorites must come from

---

[*] *Comptes Rendus,* 1838, vol. vii. p. 61.   Pouillet's formula is

$$a^{t'} = 1 \cdot 235 \, \frac{2-b}{2-b'} - 0 \cdot 489,$$

in which b'=the absorptive power by the atmosphere of the sun's heat,
    b=the absorptive power of terrestrial heat,
    t'=the temperature of the stellar heat,
    a=$1 \cdot 0077$.
    If $b=1$, its maximum, $b'=0 \cdot 2$, we find $t'=-235^\circ$ C. (-391° F.), or 71° F. above absolute zero.

beyond our atmosphere. The zodiacal light is supposed to be an evidence of meteoric matter between the earth and sun. The tails of comets are visible by some action of light upon some kind of matter. Matter in space not exposed to the rays of the sun will be at about the same temperature as the æther; but if in the rays of the sun and destitute of an atmosphere at the distance of the earth from the sun, its temperature would be very low. If present laws can be extended so far, and the earth were without an atmosphere, and the heat received were not conducted away, it has been computed that the mean temperature at the equator would be about -70° C. (-94° F.); and at the poles -221° C. *, or 114° F. above absolute zero. The last result is obtained on the supposition that the poles receive heat directly from the sun a part of the year ; it is further shown that if the poles were never exposed to the rays of the sun, the temperature would fall to that of the æther of space. But the data is not uniform, and there is too large an extension of empirical formulas to satisfy one that the above numerical results are reliable ; still they point more and more strongly to a temperature not many degrees above absolute zero.

3. By the essential heat of the æther we mean the temperature which would be indicated by a thermometer graduated from absolute zero in a room located in space beyond our atmosphere whose walls were impervious to the passage of external heat. It is the heat due to the self-agitated æther, just as air has a temperature when not exposed to the rays of the sun. If the æther be perfectly diathermanous to the sun's rays, it will receive no heat on account of the heat of the sun flowing through it, though it may be heated from other sources. As direct evidence of an extremely low temperature of space, we cite the facts in regard to the meteorite which fell at Dharmsalla, India, July 14, 1860 †. "The most remarkable thing about it was, while the mass had been inflamed and melted at the surface, the fragments gathered immediately after the fall and held for an instant were *so cold that the fingers were chilled*. This extraordinary assertion, which is contained in the report with no expression of doubt, indicates that the mass of the meteorite retained in its interior the intense cold of the interplanetary space, while the surface was ignited in passing through the terrestrial atmosphere." Since this body had been exposed to the rays of the sun, its temperature must have exceeded that of the space through which it

* Professional Papers of the Signal Service, U. S. A.: Washington, D. C. 1884, No. xii. p. 54.

† *Comptes Rendus*, 1861, tome liii. p. 1018.

passed, as well as been warmed by the heat developed at its surface, from which it may be inferred that it had been *intensely* cold. Direct investigations, given above, indicate that this temperature is less than 200° F. above absolute zero ; and we cannot assert that it is not less than 100° F. above, or even much less.

But, however low be the temperature of the æther, it cannot be absolutely cold, or, in other words, it must have a temperature above absolute zero, for otherwise it would be destitute of elasticity, and hence incapable of transmitting a wave. This is shown by eliminating V between equations (2) and (6), giving

$$c\tau = \frac{\mu}{2g\delta J}e, * \quad . \quad . \quad . \quad . \quad . \quad (21)$$

in which if $\tau=0$, e will be zero, all the other factors being finite, and if $e=0$, then $V=0$ in (2). Indeed, this principle is so well recognized in physics, that a proof in this place seems superfluous. Being unable, in the present state of our knowledge, to do more than assign the probable superior limit of the temperature, we will, for the purposes of this analysis, assume $\tau = 20°$ F., absolute, being confident that the actual value is between $\frac{1}{10}$ of and 10 times this value. This value in equation (20) gives

$$c = 46 \times 10^{11} = 4,600,000,000,000 \quad . \quad . \quad . \quad (22)$$

for the specific heat of the æther, that of water being unity. This number so vastly—we might say infinitely—exceeds that for any known gas, as to justify one, at first thought, in looking with suspicion upon the applicability of the above analysis to this medium. Assumptions in regard to the absolute temperature will scarcely improve the appearance of this number. If it be assumed that the absolute temperature be only one degree, the number in equation (22) would be only twenty times as large ; and if the absolute temperature be assumed at 1,000,000° F., the resulting specific heat would still be more than a million times as large as for hydrogen. A few considerations of other properties of the æther may aid one in being reconciled to this paradoxical result. Is the result any more incredible than the fact, everywhere admitted, that every particle of the æther, in transmitting a wave of light, continually

---

* We note that this equation shows that the specific heat for different gases under the same tension, e, and temperature, τ, varies inversely as the density ; and for the same temperature and density the specific heats c will be directly as the tension e. The more perfect gases, as hydrogen, oxygen, and air, conform nearly to this law.

makes 590,000,000,000,000 (6×10^{14} nearly) complete cycles of movements every second, for a wave-length of $\frac{1}{50,000}$ of an inch? The number of such complete movements in air for the fundamental c is only 264 ; and hence the ratio of the former to the latter of these numbers is nearly 2×10^{12}. The ratio of the specific heat given in (22) to that of hydrogen is nearly $1\frac{1}{3} \times 10^{12}$, which is not so different from that just given for the ratio of cyclical movements in a second of the æther and air. The velocity of sound in air at 493° F. above absolute zero is about 1090 feet per second ; but if the temperature could be reduced to 20° F., absolute, the law being extended so far, the velocity would be only

$$V = 109\sqrt{\frac{20}{493}} = 217 \text{ feet ;}$$

but the velocity of light is 982,000,000 feet per second, a number about $4\frac{1}{2}$ million times the former, and near a million of times that of the velocity in air under ordinary conditions. The ratio of the mass of air in a cubic foot at sea-level to that of a cubic foot of the æther as computed, far exceeds any of these ratios. The fact is, the known qualities of the æther in transmitting light and heat so far transcend those of any known terrestrial substance, that we might anticipate the fact that, in regard to magnitude, all its properties will be extremely exceptional when compared with such substances. We must accept substantially the number in equation (22), or subject this medium to different laws than those of gases.

We may deduce this result by another process ; thus, since the specific heats of different gases are as the squares of the wave-velocities in the respective substances, the other elements being the same, if the specific heat of air be 0·23, we should have for the specific heat of the æther

$$c = 0.23\left(\frac{186,300 \times 5280}{217}\right)^2 = 46 \times 10^{11},$$

as before. The correct value of the specific heat of air, 0·2375, would give over 47×10^{11}, and nearly 48×10^{11} ; but these differences are quite immaterial in this connection, the object being to check the former result, and find chiefly qualitative values.

On the other hand, in order that common air might be able to transmit a wave of the known velocity of light, its specific heat being taken constantly at 0·23, its temperature would be,

according to equation (20),

$$\tau = \frac{92 \times 10^{12}}{0 \cdot 23} = 4 \times 10^{14} \text{ degrees F.}$$

$$(= 400,000,000,000,000° \text{ F.}).$$

If the sun were composed of a substance having such specific heat, it could radiate heat at its present rate for more than a hundred millions of centuries without its temperature being reduced 1° F., exclusive of any supply from external sources, or from a contraction of its volume. We know only such substances in the sun as we are able to experiment with in the laboratory; and if there be an exceptional substance in it, we have no means at present of determining its physical properties. It is, moreover, a question whether the æther constitutes an essential part of bodies. We conceive of it only as the great agent for transmitting light and heat throughout the universe.

On account of the enormous value of the specific heat, it will require an inconceivably large amount of heat (mechanically measured) to increase the temperature of one pound of it perceptibly. Thus, if heat from the sun, by passing through a pound of water at the earth, would raise the temperature 100° F. and maintain it at, say, 600° F., absolute, it would, under similar conditions, raise the temperature of one pound of the æther, if its power of absorption be the same as that of water, $\frac{1}{46,000,000,000}$ of a degree*.

The distance of the earth from the sun being 210 times the radius of the latter, the amount of heat passing a square foot of spherical surface at the sun will be about 45,000 times the heat received on a square foot at the earth normally exposed to its rays, so that, under the conditions imposed, the temperature would not be a billionth of a degree F. higher at the sun than at the earth. This, then, is a condition favourable to a sensibly uniform temperature even if heated by the sun's rays. *We* are now inclined to admit that the æther is not perfectly diathermanous to the sun's rays, but that its temperature, however small, may be due directly to the absorption of the heat of central suns; for we begin to realize the fact that the æther may possess many of the qualities of gases, such as a molecular constitution, and hence also mass, elasticity, specific heat, compressibility, and expansibility, although the magnitude of these properties is anomalous. We have already considered its

* This illustration is rather crude, since it discards the relative volumes occupied by a pound of the respective substances.

compressibility at the surface of the sun, due to the weight of an infinite column, and found it to be exceedingly small ; now it may be possible that the expansion due to the excess of temperature of a small fraction of one degree at the surface of the sun over that at remote distances will diminish the density as much, or about as much, as pressure increased it, thereby making the density even more exactly uniform than it otherwise would be. According to what we know of refraction, it is impossible for a ray of light to be refracted in passing through the æther only,—at least, not by a measurable amount ; for not only are the density and elasticity practically uniform, but their ratio is, if possible, even more constant as shown by equations (16) and (16′). But the freedom of the æther-molecules may be constrained, or their velocity impeded, by their entanglement with gross matter, such as the gases and transparent solids ; in which case refraction may be produced in a ray passing obliquely through strata of varying densities. Neither is it believed that the æther does or can reflect light ; for if it did, the entire sky would be more nearly luminous. The rays in free space move in right lines.

The masses of the molecules in different gases being inversely as their specific heats, and as the specific heat of hydrogen is 3·4, and the computed mass of one of its molecules $\frac{11}{18} \times 10^{-29}$* of a pound, we have for the computed mass of a molecule of the luminiferous æther,

$$m = \frac{11}{18 \times 10^{29}} \times \frac{3 \cdot 4}{46 \times 10^{11}} = \frac{1}{22 \times 10^{40}} \text{ lb.} \quad . \quad (23)$$

* Stoney concludes that " it is therefore probable that there are not fewer than something like a unit eighteen (10^{18}) of molecules in a cubic millimetre of a gas at ordinary temperature and pressure" (Phil. Mag. 1868 [4] xxxvi. p. 141). According to the Kinetic theory the number of molecules in a given volume under the same pressure and temperature is the same for all gases. The weight of a cubic foot of hydrogen at the temperature of melting ice and under constant pressure being 0·005592 of a pound, and as a cubic foot equals 28,315,000 cubic millimetres, the probable mass of a molecule of hydrogen will be

$$\frac{0 \cdot 005592}{32 \frac{1}{6} \times 28,315,000 \times 10^{25}} = \frac{11}{18 \times 10^{29}} \text{ lb.}$$

Maxwell gives $\frac{46}{10^{25}}$ of a gramme $= \frac{3}{7 \times 10^{23}}$ lb., which is about $\frac{3}{5}$ the value given above (Phil. Mag. 1873 [4] xlvi. p. 468).

The difference in these results arises chiefly from the calculated number of molecules in a cubic foot of gas under ordinary conditions. Thomson gives as the approximate probable number 17×10^{25}, which is about $\frac{3}{5}$ the value given by Stoney. Thomson's value would make the mass of a molecule of æther about $\frac{1}{13} \times 10^{-40}$ of a pound, which is not much different from that found above.

The mass of a cubic foot of the æther, equation (9), divided by the mass of a molecule, gives the number of molecules in a cubic foot, which will be

$$n = \frac{2}{35 \times 10^{24}} \times \frac{22 \times 10^{40}}{1} = \tfrac{44}{35} \times 10^{16}, \quad . \quad . \quad (24)$$

which call 10^{16}. This number, though large, is greatly exceeded by the estimated number of molecules in a cubic foot of air under standard conditions, which, according to Thomson, does not exceed 17×10^{25}, a number nearly 17,000,000,000 times as large as that in equation (24) ; and yet, at moderate heights, the number of molecules in a given volume of air will be less than that of the æther.

Assuming that air is compressed according to Boyle's law, and is subjected to the attraction of the earth, equation (15) will give the law of decrease of the density. Taking the density of air at sea-level at $\frac{1}{400}$ of a pound per cubic foot, $e_0 = 14 \cdot 7$ lb. per square inch, $r = 20,687,000$ feet, equation (15) becomes

$$\delta = \tfrac{1}{400} \times 10^{-345 \frac{z}{r+z}}. \quad . \quad . \quad . \quad . \quad (25)$$

If $z = \infty$, $\delta = \frac{1}{400} \times 10^{-345}$, which would be the limit of the density, and it is a novel coincidence that this limit is nearly identical with the value found for the density at the height of one radius of the earth according to the ordinary exponential law wherein gravity is considered uniform[*].

If the number of molecules in a cubic foot follows the same law, then at the height z there will be

$$17 \times 10^{-345\frac{z}{r+z}+25} \quad . \quad . \quad . \quad . \quad (26)$$

molecules per cubic foot. Similarly, the value of the length of the mean free path would be[†]

$$2 \times 10^{345\frac{z}{r+z}-6} \text{ inches.} \quad . \quad . \quad . \quad (27)$$

By means of these values, the following table may be formed :—

---

[*] The ordinary exponential law results from dropping $\frac{z}{r}$ compared with unity in equation (15), giving

$$\delta = \delta_0 \epsilon^{-\frac{z}{26221}} = \delta_0 10^{-\frac{z \text{ ft.}}{60387}} = \tfrac{1}{400} \times 10^{-\frac{z \text{ miles}}{11 \cdot 44}},$$

in the last of which, if $z = 3956$, the exponent becomes 345.

[†] Phil. Mag. 1873 [4] xlvi. p. 468.

Height.		Density or tension, that at the earth being unity.	Number of molecules in a cubic foot.	Length of the mean free path.
Fractional parts of earth's radius.	Approximate in miles.			
0	0	1	17×10^{25}	2×10^{-6} inch
$\frac{1}{79}$	50	$10^{-4 \cdot 3}$	$17 \times 10^{20 \cdot 7}$	$2 \times 10^{-1 \cdot 7}$,,
$\frac{1}{39}$	100	$10^{-8 \cdot 4}$	$17 \times 10^{16 \cdot 6}$	$2 \times 10^{2 \cdot 4}$,,
$\frac{1}{20}$	200	$10^{-16 \cdot 4}$	$17 \times 10^{8 \cdot 6}$	792,000 miles
$\frac{1}{14}$	282	10^{-23}	17×10^{2}	31×10^{11} ,,
$\frac{1}{10}$	395	10^{-31}	17×10^{-6}	31×10^{19} ,,
$\frac{1}{5}$	800	10^{-57}	17×10^{-32}	31×10^{45} ,,
1	3956	10^{-172}	17×10^{-147}	31×10^{160} ,,
2	7912	10^{-230}	17×10^{-205}	31×10^{218} ,,
∞	∞	10^{-345}	17×10^{-320}	31×10^{333} ,,

The numbers in the third column multiplied by $\frac{1}{400}$ will give the density (or mass per cubic foot) at the respective altitudes; and the same numbers multiplied by 15 (or more accurately 14·7) will give the tension per square inch. According to this law, at an elevation of 300 miles the density of the atmosphere will be somewhat less than the density of the æther as given by equation (9).

To find the height at which the tension of the atmosphere, according to the above law, will be the same as that of the æther, we have, by means of equations (11) and (25), substituting in the latter 2116 for $\frac{1}{400}$,

$$ 2116 \times 10^{-345 \frac{z}{r+z}} = \frac{4}{10^{8}}, $$

which solved gives

$$ z = \frac{r}{31 \cdot 24} = 126 \cdot 6 \text{ miles,} $$

so that at the height of 127 miles the tension would be less than that of the æther, the temperature being uniform.

The mean free path according to the above law, in which gravity varies as the inverse squares, is less, and for great heights much less, than would be found according to the ordinary exponential law. Thus Crookes states that the mean free path of a molecule at the height of 200 miles is about

2 G 2

10,000,000 miles[*]; but according to the above law it becomes
about 792,000 miles.

If a cubic inch of air at sea-level were carried to the height
of $\frac{1}{7}$ the radius of the earth, and then allowed to expand freely,
so as to become of the computed density of the atmosphere at
that point, it would fill a space of $4 \times 10^{28\cdot12}$ cubic miles, or a
sphere whose radius is 2,398,000,000 miles, which is nearly
equal to the distance of the planet Neptune from the sun ;
and there would be less than one molecule to the mile.   Such
are some of the results of extending a law to extreme cases
regardless of physical limitations, or of the imperfection of
the data on which it is founded.   For instance, a uniform
temperature is assumed, and, impliedly, an unlimited divisi-
bility of the molecules.   The latter is necessary in order to
maintain a law of continuity.   But modern investigations
show that not only air, but all the gases, are composed of
molecules of definite magnitudes whose dimensions can be
approximately determined ; and hence, if there be only a few
molecules in a cubic foot, and much less if there be but
one molecule in a cubic mile, it cannot be claimed that the
gas will be governed by the same laws as at the surface of
the earth.

To find the Height of the Atmosphere.—The atmosphere will
terminate at that height where the vertical repulsive force
equals the weight of the particles in the topmost layer.   As a
first approximation, conceive that the molecules are arranged
in horizontal layers and vertical columns, in a prism whose
base is one square foot, and whose height extends to the
height of the atmosphere ; the base of each column of mole-
cules being one of the molecules in the base of the prism.
Considering the number of molecules in a cubic foot of air
at standard conditions as 17×10^{25}, and the weight of the
same as ·08 of a pound, we have for

$$\text{the weight of one molecule of air} = \frac{8}{17 \times 10^{27}} \dagger. \quad . \quad (28)$$

The number of molecules along one edge of the bottom
layer will be $\sqrt[3]{17 \times 10^{25}}$ nearly ; and the number in the
bottom layer the square of this number, or $170^{\frac{2}{3}} \times 10^{16}$,
which, according to the hypothesis, will be the number in

---

† This may be used as a unit for measuring the mass of a cubic foot
of the æther.   Thus, dividing the value in equation (10) by that in (28)
gives 4250 ; or the mass of æther in a cubic foot is 4250 times the mass
of one molecule of air.

the top layer ; and this multiplied by the weight of one mole-
cule will give e, the weight in the top layer ; and equation
(14) will give (the temperature of the column being considered
uniform)

$$14 \cdot 7 \times 144 \times 10^{-345 \frac{z}{r+z}} = \frac{170^{\frac{2}{3}} \times 10^{16} \times 8}{17 \times 10^{27}} ;$$

$$\therefore \quad z = \frac{r}{23 \cdot 35} = 169 \text{ miles.} \quad \cdots \quad (29)$$

But the temperature is far from being uniform.   In regard
to a definite mass of a gas, we have the well-known relation

$$\frac{e}{\delta\tau} = \frac{e_0}{\delta_0\tau_0} = \text{a constant} = \frac{pv}{\tau}, \quad \cdots \quad (29')$$

where $p = e =$ the pressure on the base of a prism, and $v =$ the
volume.

The value of δ from this equation substituted in (13) gives

$$\frac{de}{e} = -g\frac{\delta_0}{e_0} \cdot \frac{\tau_0}{\tau} dz. \quad \cdots \quad (30)$$

But with τ an unknown variable this cannot be integrated.
If $\tau = \tau_0$ we at once have equation (14).   The relation between
τ and z is unknown, if indeed there be any algebraic relation
between them.   It is, however, known that, as a general fact,
the temperature decreases with the elevation ; although local
causes and air-currents often cause this law to be reversed
for moderate heights.   The best that can be done, in this
case, is to find an expression that will represent, approxi-
mately, the mean values of the temperature.   It is usually
assumed that the average temperature at the earth is about
59° F. or 60° F., and that for latitudes of, say, 40° N. to
40° S. the perpetual frost-line is from 14,000 to 16,000 feet
above sea-level ; and observations indicate that the *rate* of
decrease of temperature decreases with the height.   The last
fact is suggestive of an exponential law ; hence assuming

$$\tau = \tau_0 \epsilon^{-\frac{z}{a}}, \quad \cdots \quad \cdots \quad (31)$$

and making $\tau = 493°$ F., absolute, at the height $z = 15,840$ feet
and $\tau_0 = 520°$ F., absolute, we find $a = 296,000$ (or 56 if z be
in miles), and our equation becomes

$$\tau = 520 \, \epsilon^{-\frac{z \text{ miles}}{56}}. \quad \cdots \quad \cdots \quad (32)$$

This gives

Height, miles.	τ, absolute.	Fahr. scale.	Glaisher's observations *.
0	520° F.	59° F.	59° F.
1–5	518	57	
2–5	515	54	
3–5	513	52	
4–5	512	51	
1	510	49	41
2	501	40	32
3	493	32	18
4	484	23	8
5	475	14	− 2
6	467	6	
7	458	− 3	−11·8
50	212	−249	
75	136	−325	
100	87	−374	
120	65	−396	
150	36	−425	
224	9	−452	

The temperatures given in twenty-five or more reports of balloon ascensions, not only give values the mean of which is fairly represented by the celebrated seven-mile ascent of Mr. Glaisher, but his figures, given in the fourth column of the table, represent a more uniform law than is common in such reports. Our computed values exceed his observed values at all points except at the surface of the earth, where they agree. In this ascent he reached the point of freezing at the height of two miles, which is lower than the average, as determined by many observations; and therefore it appears that equation (31) probably represents the general law better than this single set of observations. The effect, however, of the exponential law is scarcely perceptible within the limits of observation ; for the exponent of ϵ is so small for elevations under seven miles, that it makes the law of decrease of temperature nearly uniform with equal increments of elevation. Thus, omitting fractions, the computed decrease for the first mile is 10°, and the average for seven miles is nearly 9° ; but to assume a uniform decrease throughout the column limits the height of the column independently of pressure or other conditions, for it could not extend beyond the point of absolute zero. There is no objection to applying such a law

* ' Travels in the Air,' by James Glaisher, F.R.S., p. 50.

provided it can be shown to be true—a condition which, at present, is not accepted.

Substituting τ from (31) in (30), and integrating between the limits of z and $z=0$, gives

$$e = e_0 \, \epsilon^{-\frac{ag\delta_0}{e_0}(\epsilon^{\frac{z}{a}}-1)} ; \quad \ldots \quad (33)$$

which ultimately will equal the weight of the molecules in the top layer. Hence, substituting numbers, we have

$$2116 = \frac{8 \times 170^{\frac{2}{3}} \times 10^{16}}{17 \times 10^{27}} \, \epsilon^{\frac{296000 \times 08}{2116}(\epsilon^{\frac{z}{56}}-1)} ;$$

which gives

$$z = 86 \text{ miles.} \quad \ldots \ldots \ldots \quad (34)$$

It is evident that the very low temperature of the higher portions of the column will shorten very much the hypothetical column of uniform temperature ; but there are other conditions which will modify the preceding analysis. The assumptions in regard to layers and columns would not be realized even under statical conditions, and much less for the conditions in nature. Statically, the molecules would arrange themselves more like shot in a pile, each being over the space between the molecules in the layer below, instead of over a molecule. This arrangement would give a less number in the horizontal layers than assumed above. But the hypothesis of constancy in the number of molecules in the layers is open to greater objections. For the distance between the molecules will increase with the elevation on account of the diminution of the pressure of that part of the column above the point considered, and the elastic force will be correspondingly diminished ; while, horizontally, in the plane of a layer of the molecules, the elastic force would remain constant. In other words, in the medium arranged as assumed the tension would not be the same in all directions, and hence would be in unstable equilibrium. As a refinement, we notice that in every heavy fluid the downward pressure at every point exceeds the upward by the weight of a molecule.

Considering, now, that the molecules in the hypothetical layers are distributed uniformly throughout the spaces immediately beneath them, the number in the new top layer will be less than in the former case, and the column will rise to a greater height, and hence will exceed 86 miles ; and, in turn, the new column would need another correction, and so on. Assuming that the number in the top layer is 10^{10}, and that the vertical component of the elastic forces follows the law of

equation (33), we find

$$z = 95 \text{ miles};$$

and if the number in the top layer be 10^4, we find $z=104$ miles, and for *one* molecule, $z=110$ miles. In a similar manner it would be legitimate to assume that the column was capped by a fraction of a molecule, for that would be equivalent to one molecule at the top of a column having a base of several square feet. We are unable to determine where this process would end in nature; and hence this analysis fails to fix definitely the extreme height of the atmosphere, even for statical conditions.

Assuming that the distance between the contiguous molecules would be inversely as the third root of the densities of the medium, as they would be with sufficient accuracy where the number of molecules in a cubic foot is immense, we have, after substituting e, equation (33), and τ, equation (31), in $(29')$,

$$\frac{\delta}{\delta_0} = \epsilon^{\left[\frac{z}{a} - \frac{ag\delta_0}{e_0}(\epsilon^{\frac{z}{a}}-1)\right]} = \frac{d_0{}^3}{d^3},$$

where d_0 is the distance between contiguous molecules at sea-level and d the corresponding distance at the height z.   Hence

$$d = d_0\left[\epsilon^{\frac{ag\delta_0}{e_0}(\epsilon^{\frac{z}{a}}-1)-\frac{z}{a}}\right]^{\frac{1}{3}} \quad . \quad . \quad . \quad . \quad (35)$$

If $d_0 = \dfrac{18}{\sqrt[3]{170 \times 10^8}}$, $\dfrac{ag\delta_0}{e_0} = 11{\cdot}19$; we have

$$
\begin{array}{lll}
\text{for } z = 86 \text{ miles}, & d = \tfrac{1}{95} \text{ of an inch}, \\
\text{,, } z = 95 \text{ ,,} & d = 4{\cdot}5 \text{ inches}, \\
\text{,, } z = 104 \text{ ,,} & d = 11{\cdot}4 \text{ ,,}
\end{array}
$$

These values of d are greatly in excess of the distances between contiguous molecules in the horizontal layers, according to assumed conditions. Thus, at the height of 104 miles, it was *assumed* that there were 10^2 molecules on the side of a square foot, in which case the distance between contiguous molecules would be about $\frac{1}{8}$ of an inch instead of 11 inches as above. These results ought not to agree exactly, for one analysis assumes that the atmosphere terminates with each assumed number of molecules, while the other assumes that the law is continuous to any height. It is apparent that the laws represented by equations (33) and (35) both become practically discontinuous at a height at or less than 95 miles. For the sake of giving definiteness to the following remarks, we will assume that the mean height for statical conditions is

95 miles. But the conditions in nature are not statical. The changes in temperature in the column will be continually increasing or decreasing its height; the air-currents also operate to change it, first by increasing or decreasing the temperature from the mean at considerable heights, and, secondly, by operating dynamically to push the top of the column upward; the aerial tides may operate to raise the column still higher, and the molecules themselves are supposed to be flying with great rapidity in all directions. An increase of temperature of one tenth the mean value, which at the earth's surface would be about 49° F., would elongate the column about ten miles, and a corresponding decrease would shorten it about the same amount, making it 105 miles in the former case and 85 miles in the latter. The effect of air-currents and aerial tides cannot be so definitely calculated; but it is safe to assume that they may produce a much greater increase of height above the mean than they will depression below the mean ; just as in a highly agitated sea, the depressions below the mean surface-level may be small compared with the height above the same level to which the spray from the top of a wave may be thrown. It seems possible, therefore, that when the temperature, air-currents, and aerial tides conspire to depress the column, the extreme height of the atmosphere may be reduced to less than 85 miles; and when they conspire to elevate it, it may possibly rise to a height exceeding 120 miles.

If it be certain, as is assumed, that the meteors are rendered incandescent by atmospheric friction, and the extreme height at which they are visible could be determined by direct observation, it would fix a height less than the extreme height of the atmosphere, independent of other physical considerations; but the movement of these bodies is so extremely rapid that it is impossible to determine their height with astronomical precision. Still computations by Professor Herschel give a height of about 118 miles[*], and Professor Newcomb estimates it to be about 100 miles[†]. It is possible that a meteor would sometimes become inflamed by penetrating the atmosphere

---

[*] Professor A. S. Herschel gives the height of twenty meteors varying from 40 to 118 miles. 'Nature,' vol. iv. p. 504.

[†] Newcomb says:—" The lightning-like rapidity with which the meteors darted through their course rendered it impossible to observe them with astronomical precision; but the general result was that they were first seen at an average height of 75 miles and disappeared at a height of 55 miles. There was no positive evidence that any meteor commenced at a height greater than 100 miles. These phenomena seem to indicate that our atmosphere really extends to a height of between 100 and 110 miles." 'Popular Astronomy,' 1878, p. 389.

only a few miles, for although the atmosphere in the upper regions is extremely rare, yet the actual number of molecules in a cubic foot is large. Thus, according to our analysis, for statical conditions, the topmost cubic foot of the 104-mile column would contain about 1,000,000 molecules; and at the height of 95 miles it would contain about 1,000,000,000,000,000 molecules; so that if the relative velocities of the meteor and air be 20 miles per second, the meteor would encounter an *enormous* number in the twentieth or even the hundredth part of a second, after first entering the atmosphere.

The height of the auroral arch—supposed to be within our atmosphere—has been computed to be from 33 to 1000 miles (see article "Aurora," *Encyc. Brit.*). But it has been shown by experiment, that a vacuum may be produced through which an electrical discharge cannot be passed, and yet the atmosphere at the height of 150 miles under the most favourable condition, that of uniform temperature, is vastly more rare than the most perfect vacuum ever produced by the most perfect Sprengel pump; and at the height of 200 miles under the same conditions the vacuum would be some 10,000,000 times as great as the most perfect vacuum yet made; while, according to the probable law of the decrease of temperature with the elevation, and in accordance with the probable mass of a molecule of air, the extreme height falls far short of 150 miles. It is evident, therefore, that the assumed determination of the height of the atmosphere by means of the auroral arch is, to say the least, unreliable[*].

We have pursued this digression in regard to the atmosphere partly for its own sake and partly to show, by way of contrast and accumulative evidence, that the æther is a substance entirely distinct from that of the atmosphere,—that the former cannot be considered as the latter greatly rarefied, as some have supposed. Admitting the validity of the preceding discussion, some of the distinctive properties are:—

1. The different modes of the movements of the molecules in the two substances in the propagation of a wave; in one the motion being a to-and-fro movement and in the other a transverse movement. These are distinctions recognized by the best writers upon the subject, and are especially noticed by Maxwell in an article on Ether in the *Encyclopædia Britannica*.

2. It is impossible for a wave to be transmitted in air with the known velocity of light, unless its temperature be increased

[*] Some writers incline to the view that the aurora is due to a cosmic rather than a terrestrial origin. 'Science,' 1885, p. 395.

millions of millions of degrees Fahrenheit above the standard temperature; but such a wave is transmitted in the æther although its temperature is far less than has ever been produced by artificial means.

3. The ratio of the elasticity to the density in the æther is exceedingly large compared with the same ratio in air. The temperature of air being taken at 60° F. and the æther at 20° F., absolute, the ratio is, with sufficient accuracy,

$$\left(\frac{980,000,000}{1090}\right)^2 = 8 \times 10^{11} \text{ nearly.}$$

4. The specific heat of the æther is, at least, many million times that of air, or of any other known gas.

5. The atmosphere is of variable density, elasticity, and temperature, while the æther is well-nigh isometric throughout space in regard to each of these elements.

6. A molecule of æther is well-nigh infinitesimal compared with one of air.

7. Air is attracted to a planet with such a relative force, that its extreme height is only a few miles.

8. The ratio of the density to the elasticity of the æther is constant; but in the atmosphere, on account of the decrease of temperature with the elevation, the density decreases less rapidly than the elasticity, as may be seen by comparing the first part of equation (35) with equation (33): we have

$$\frac{\delta}{\delta_0} = \epsilon^{\frac{z}{a}} \cdot \frac{e}{e_0}.$$

On this account a wave would be propagated with less velocity in the higher regions of the atmosphere than in the lower, while a wave in the æther has a sensibly uniform velocity throughout space.

The question may arise, May not the resistance of the æther drag away the remote molecules of the atmosphere, and so scatter them in space along the path of the earth's orbit? Assuming that the atmosphere is moving with the earth through space at the rate of 20 miles per second (which exceeds the actual velocity), and that the resistance of the æther is measured in the same manner as for fluids, we have for the resistance $R = kwa \dfrac{v^2}{2g}$, where v is the velocity of a molecule of air, a is meridian section, w the weight of a unit of volume of the æther, and k a coefficient depending upon the form of the body. Making $k = 1$, which is greater than its

actual value, and $a=\dfrac{1}{10^{17}}$ feet, which, again, is in excess of the true area, w the value in equation (10), we find that

$$R=\frac{2}{10^{24}}\times\frac{1}{10^{17}}\times(20\times5280)^2\cdot\frac{1}{64\cdot4}=\frac{1}{10^{33}}\text{ of a pound nearly.}$$

The attractive force of the earth for a molecule of air is given in equation (28), and hence the attraction of the earth for a molecule of air will exceed 500,000 times the resistance of the æther; hence the molecules accompany the earth in its orbit as certainly as does the moon, and are more rigidly bound to it than is its satellite.

The Kinetic energy of a molecule of air at standard conditions is about

$$\frac{1}{2}\cdot\frac{8}{32\cdot2\times17\times10^{27}}1600^2=\frac{2}{10^{23}}\text{ foot-pound;}$$

and of the æther, according to our results, about

$$\frac{1}{2}\cdot\frac{1}{22\times10^{40}}(273,000\times5280)^2=\frac{1}{2\times10^{23}}\text{ foot-pound;}$$

which results are nearly the same; but in a pound of the æther there is some 100,000,000,000 times the Kinetic energy of a pound of air.

Considering the terrestrial atmosphere as equivalent to one of uniform density and $5\frac{1}{2}$ miles high, each of whose molecules has a mean square velocity of 1600 feet per second, and the æther of uniform density each of whose molecules has the mean square velocity of 286,000 miles per second, a rough approximation shows that the Kinetic energy of the æther in a sphere whose radius is 92,000,000 miles (nearly the distance of the earth from the sun) will be only about 100,000 times that in our atmosphere.

The mean free path of a molecule of gas as given by Loschmidt is

$$l=\frac{\text{combined volume of the molecules}}{\text{volume of the gas}\times\frac{1}{8}\text{ the diameter of a molecule}},$$

and by Maxwell,

$$l=\frac{\mu}{\rho}\cdot\frac{1}{v}=3\frac{\mu}{\rho}\cdot\frac{z}{\gamma V};$$

(the last member of which we have added) in which ρ is the density of the gas, μ the coefficient of internal friction, and v the velocity whose square is the mean of the squares of the actual velocities of the molecules. In regard to the æther, these equations contain at least three unknown quantities, l, μ, and the diameter of a molecule, and hence they cannot be

completely solved. Comparative results, however, may be found by assuming that the density of the molecules of æther equals those of hydrogen, or is any multiple thereof; for then the diameter of a molecule of the æther might be found (that of hydrogen being $5 \cdot 6 \times 10^{-10}$ of a metre); and the combined volume in a cubic foot will equal the number of molecules in a cubic foot multiplied by the volume of one molecule, and hence will be found the length of the mean free path and the coefficient of internal friction.

We conclude, then, that a medium whose density is such that a volume of it equal to about twenty volumes of the earth would weigh one pound, and whose tension is such that the pressure on a square mile would be about one pound, and whose specific heat is such that it would require as much heat to raise the temperature of one pound of it $1°$ F. as it would to raise about 2,300,000,000 tons of water the same amount, will satisfy the requirements of nature in being able to transmit a wave of light or heat 186,300 miles per second, and transmit 133 foot-pounds of heat-energy from the sun to the earth each second per square foot of surface normally exposed, and also be everywhere practically non-resisting and sensibly uniform in temperature, density, and elasticity. This medium we call the Luminiferous Æther.

XLVIII. *A Determination of the Ohm.* ### By Prof. F. Himstedt[*].

THROUGH the means placed at my disposal by the Government of the Grand Duchy of Baden, for the determination of absolute resistance, I have been enabled to carry out a determination of the Ohm according to the method recently published by me[†]; and beg permission to lay an abstract of my results in the following paper before the Royal Berlin Academy.

According to the above-mentioned method, the constant divergences of the magnet in the same galvanometer are observed—produced in the one case by means of induction-currents passing in the same direction through the galvanometer at the rate of n per second; in the other case by means of a constant current whose strength is a known fraction of the inducing current. Let us call the observed angles of divergence α_1 and α_2, the required resistance r will be found

---

* Translated from the *Sitzungsberichte der k. Pr. Akad. d. Wissens.* Berlin, July 23, 1885.
† Wied. *Ann.* Bd. xxii. S. 281 (1884).

(as is elsewhere more fully stated) from the formula

$$r = n \cdot V \frac{\tan \alpha_2}{\tan \alpha_1}, \quad \cdots \cdots \quad (1)$$

in which V expresses the potential of the induction-coils here used towards one another.

If we take as inducing coil a solenoid with only one layer of wire, in comparison with whose length both its own radius and the dimensions of the inducing coil are insignificant, we get

$$V = 4\pi^2 R^2 K \cdot b \cdot (1 + 2a);$$

whence follows :—

$$r = 4\pi^2 R^2 K \cdot b \cdot n(1 + 2a) \frac{\tan \alpha_2}{\tan \alpha_1}. \quad \cdots \quad (2)$$

R expresses here the radius of the solenoid, K the number of convolutions in a unit of length, b the total number of convolutions of which the induction-coil consists, and $2a$ a term of correction which expresses the action of the ends of the solenoid.

According to the experiments described below, the value of $2a$ was always less than $0 \cdot 03$; so that for the determination of r only the exact measurement of the quantities R, b, n, K, and $\frac{\tan \alpha_2}{\tan \alpha_1}$ were taken into account.

The advantages of this manner of experimenting are that the number of the quantities to be ascertained is a comparatively small one, and that all those quantities are omitted which require great care in their accurate determination. I place under this heading the constants and variations of terrestrial and of rod magnetism, the coefficients of induction of the surfaces of convolution of the wire-bobbin of many superposed layers, the reduction-factor of the galvanometer, the moment of inertia and logarithmic decrement of magnets in oscillation, and, more especially, the exact determination of the resistance of copper wires which are often not all in the same room, and whose temperature can only be approximated to from the temperature of the surrounding air*.

All length-measurements in the following treatise were compared with a standard which Privy-Counsellor Förster was good enough to correct at the Normal-Standards Commission in Berlin by means of the normal metre standard.

The measurements of time were carried out by means of

* Compare Roiti, *Nuovo Cim.* ser. 3, vol. xv., " Diterminazione della resistenza elettrica di un filo in missura assoluta."

a ship's chronometer of Bröcking's, which was rated by observation.

The solenoid is wound round upon a wooden block repeatedly coated with glue, such as are used in orchestrions. It was made in the year 1868, and was again planed down and polished on the lathe in May of last year. Its diameter was determined in three different ways, which were so chosen that it was possible at the same time to ascertain that the section of the drum sufficiently approximated to a circle, and that the whole block was a cylinder. They were :—

1. Every six diameters of the same section were compared, by means of a micrometer-screw at thirteen equidistant points along the length of the block, with a glass rod measuring 23·3264 centim. in length*.

The diameters found were:—

Lowest value.	Highest value.	Mean.
centim.	centim.	centim.
23·3193	23·3286	23·3248

2. The circumferences were measured by means of strips of paper at thirteen equidistant points, whence the calculated diameters were:—

Lowest value.	Highest value.	Mean.
centim.	centim.	centim.
23·3186	23·3252	23·3229

3. The diameter was reckoned from the length of the wire wound round it. During the winding the thickness of the wire was at the same time measured at 332 points by means of a microscope with ocular micrometer, and found to be 0·0472 centim. The diameter of the block was found to be

$$D = 23\cdot3262 \text{ centim.}$$

The measurements in No. 2 were repeated after the winding, D = 23·3190 centim., and were carried out again after each determination, both with strips of paper and a steel-band measure, D = 23·3194 centim. and 23·3204 centim. As the mean of all the measurements, we get for radius R the formula (2),

$$R = 11\cdot6846 \text{ centim.}$$

The isolation of the wire coils was tested by means of Hughe's induction-scale †.

The number of convolutions was 2864 ; they covered the drum to a length of 135·125 centim.

* The length of this glass rod was determined at the Normal-Standards Commission in Berlin.

† *Cf.* Rayleigh, Phil. Trans. 1884, vol. clxxv. p. 419, " On the Electrochemical Equivalent of Silver."

We get then

$$K = \frac{2864}{135 \cdot 125}.$$

The induction-coil is also wound round wood, and consists of 3848 convolutions in 15 sections, which can be combined at pleasure. The width of the bobbin was 4·01 centim. The mean radius of each section was reckoned from the circumferences of the separate layers of wires, which had been measured by means of strips of paper. To test the isolation of the coils, and to possess a control over the paper-measurements, the mean radius of each section of the wider one was determined by Von Bosscha's method [*]. As, however, the dimensions of the bobbin are only expressed in the term $2a$ of formula (2), a mistake of one per cent. would only falsify the value of r by at most 0·0003.

The resistance r, which has to be determined in absolute measurement, amounted either to 1 or $\frac{1}{2}$, or 2 Siemens units, and was composed of 2 Siemens units (by Siemen and Halske), nos. 3618 and 3619, which were used either singly or parallel, or behind one another. These were made fast in metal cases, which were filled with oil, and stood in a large bath of the same. Both before and after the experiments, both standards were compared with a third unit, and with each other.

The thermometers were divided into one-tenths of a degree, and were three times compared carefully with the standard thermometers of the Physical Institute.

The interruptor was driven by a toothed wheel [†]. For determining n, the number of interruptions, a counter was made fast to the axis of rotation, by means of which $\frac{1}{60}$ of a revolution could be directly read off.

At least 700 revolutions were counted during each experiment, so that the necessary approximation of 0·01 per cent. was easily attained. The apparatus worked very evenly, so that the divergences of the galvanometer were constant throughout.

This appears to me an advantage that this interruptor possesses over that used by Herr Roiti [‡]; and I believe that the discrepancies between his separate observations are due, if not entirely, at least in a great measure, to the unequal action of the "Schmidt" water-motor used by him.

---

[*] Wiedemann, *Elec.* iii. p. 213.
[†] F. Himstedt, "Zwei Verschiedene Formen eines selbstthätigen Disjunctors," Wied. *Ann.* vol. xxii. p. 276 (1884).
[‡] Cap. I. page 11.

The galvanometer was not artificially damped. The position of rest of the needle was determined from its maximum divergence. The divergences to be observed, α_1 and α_2, were never less than 800 millim. on a scale 4 metres distant, and were always within a few scale-divisions of each other; so that for the reduction to arcs an approximate knowledge of the distance of the scale was enough. All connecting-wires were covered with caoutchouc and twisted lightly together; all the current-reversers, &c. were made of paraffin and sealing-wax.

Altogether, sixty-seven experiments were made; only the solenoid is common to them all.

Here the only variation possible was that the induction-bobbin could be placed 10 centim. further towards either end, instead of in the middle. All other components of the apparatus were altered in each experiment to a considerable extent. The sections of the induction-coil were taken either separately or in combinations of 2–5, corresponding to which the number of the intermittences was 5–13 per second. The strength of the inducing current was from 0·0005 to 0·01 ampère. The sensitiveness of the galvanometer was con- siderably alterable. The time taken by the oscillations of the needle was from 15 to 34 seconds.

To ascertain if the induction-current passing through the galvanometer produced any other cross-magnetization of the needle, besides constant currents of otherwise equal galvano- metric action, by which the relation $\dfrac{\tan \alpha_2}{\tan \alpha_1}$ would be rendered unreliable, several experiments were made with magnets of a diameter of 0·6 centim., those used in the above-mentioned experiments being hardly 0·1 in diameter. No difference was observed after a certain number (43) of experiments had been made; the interruptor was fitted up afresh, and all con- necting-wires as well as current-reversers renewed.

As the following results tally with the former, it may be assumed that the isolation was perfect.

The whole plan of experimenting is based on the constancy of the source of electricity, be this periodic, as in the observa- tions by means of induction-currents, or continuous, as in the measurement by means of the constant current. Means had therefore to be taken to meet the final objection that errors might arise through possible polarization in the battery. With this object, I used as sources of the current:—

1. 1 to 4 Daniell's elements.
2. Two points of a wire-resistance connecting a number of Daniell's or Bunsen's elements.
3. A thermo-element.

All sources produced the same result.

The mean of all experiments performed was

1 Siemens unit = 0·94356 ohm ;

or, one ohm is equivalent to the resistance of a mercury-column having a section of 1 square millim. and a length of 105·98 centim. at 0° Centigrade.

Of the values determined,

the lowest was 1 Siemens unit = 0·94323 ohm,
the highest was 1 Siemens unit = 0·94380 ohm.

XLIX. *On the Molecular Theory of Galvanic Polarization. By* J. Larmor, *Fellow of St. John's College, Cambridge* *.

1. IT was first pointed out by Varley and Sir W. Thomson that the polarizing action of a galvanic cell may be explained by considering the cell to act as an electrical condenser of very large capacity. The mechanism of this action has since been examined in detail, especially by Helmholtz †.

In the polarization of a water-voltameter with platinum plates for electrodes, the action according to Clausius's well-known molecular theory consists in the transfer through the fluid of the temporarily dissociated hydrogen and oxygen constituents under the action of the electric force ; so that in the course of time a layer of hydrogen particles with their positive charges accumulates in the immediate neighbourhood of the kathode plate, and the complementary layer of oxygen particles with their negative charges at the anode.

Each of these layers will form a sheet, with positive or negative charge, lying close to the metal plate. On the plate will therefore appear an equal and opposite charge by induction. There is thus a double electric layer formed at each electrode ; the charged particles forming one side of it being prevented from coming up to and discharging themselves in contact with the metal, in obedience to the electrical attraction, by chemical forces of repulsion.

A double layer of this kind forms an actual condenser, whose capacity is inversely proportional to the distance between its faces. And Gauss's well-known theorem relating to magnetic shells shows, when applied to this case, that the effect of such a condenser is to cause a sudden rise or fall of potential in passing through it without producing any change in the distribution of the electric force in the neighbourhood.

---

* Communicated by the Author.
† See his *Wissenschaftliche Abhandlungen*, vol. i., section *Galvanismus*, and his Faraday Lecture in the Journal of the Chemical Society for 1882.

The notion of a condenser, therefore, gives a complete account of the principal feature of the galvanic polarization.

Direct measures of the charge by Kohlrausch showed that on dividing this polarization-fall of potential equally between the anode and kathode plates, the distance between the faces of the condenser comes out to be about the fifteen-millionth part of a millimetre; while more careful observations by Helmholtz on cells in which absorbed gases have been removed from the fluid, give the greater value of a ten-millionth of a millimetre. And Helmholtz makes out the very important fact that for all electromotive forces which do not exceed a certain moderate value, the capacity, and therefore the distance of the surface-layers, is very sensibly constant[*].

2. The most accurate and convenient method of observing the polarization at the common surface of two liquids is probably the electro-capillary method invented and applied by Lippmann.

When a surface of separation can persist between the fluids, the energy, reckoned as potential, of pairs of particles close to the surface must exceed that of the same particles when in the interior of their respective fluids. The difference may, as Gauss pointed out, be reckoned as surface-energy, and specified by its amount per unit area of surface. If T represent this amount, it follows, as is well known, that the forces which arise from it may be represented by a surface-tension equal to T across each unit of length, tending to contract the surface in all directions.

Now, if the common surface is polarized with constant charges $+Q$ and $-Q$ on its two faces, there will exist an additional *electrical* energy, which is also reckoned by its amount per unit surface, and whose total value is

$$E = \tfrac{1}{2}QV,$$

or, what is the same,

$$E = \tfrac{1}{2}\frac{Q^2}{CS};$$

where S is the area of the surface and C is its electrical capacity per unit area.

The effect of this surface-energy will therefore, the system being conservative, be represented by a surface-tension T', where

$$T' = \frac{dE}{dS},$$

$$= -\tfrac{1}{2}\frac{Q^2}{CS^2},$$

$$= -\frac{E}{S};$$

---

[*] Faraday Lecture, p. 296; *Wissen. Abh.* i. p. 858.

i. e. is equal to the electrical surface-energy per unit area of the surface, with negative sign.

The effect of the galvanic polarization will therefore be to diminish the capillary surface-tension by this amount $\dfrac{\mathrm{E}}{\mathrm{S}}$.

In the actual case in which the polarization is maintained by a battery, the difference of potential V between the faces of the condenser is what remains constant; and the system is no longer conservative, because the battery can be drawn upon; we have then

$$\mathrm{E} = \tfrac{1}{2}\mathrm{CSV}^2,$$

and

$$\frac{d\mathrm{E}}{d\mathrm{S}} = \tfrac{1}{2}\mathrm{CV}^2,$$

$$= \frac{\mathrm{E}}{\mathrm{S}};$$

therefore $d\mathrm{E} = -\mathrm{T}'d\mathrm{S}$;

i. e. this force T′ now acts so as to *increase* the total energy of electrification E, and is measured by its *rate of increase* per unit extension of area; for the work done by the contractile force T′ in an extension of surface $d\mathrm{S}$ is equal to $-\mathrm{T}'d\mathrm{S}$, which is now the increment of the energy, but under the previous conditions was its decrement.

It follows that under these circumstances the battery is drawn upon for an amount of energy equal to *twice* that required to do the electrical work of extension, viz. the energy required to do this work together with the equal amount used up in increasing E, as has just been found. This is a particular case of a general theorem of Sir W. Thomson's. We have gone into the matter here to show the consistency of the propositions which make the capillary surface-tension equal to the rate of increase of the *ordinary* surface-energy per unit extension, while the electric surface-tension is equal to the rate of decrease of the electrical surface-energy per unit extension.

Once the surface-tension becomes negative, a free surface becomes unstable, and therefore practically impossible. We notice therefore that, as the polarization is made stronger and stronger, this state of affairs would finally supervene were not the polarization previously relieved by electrolytic separation of the charged layer.

3. We have proved that the surface-tension is diminished by galvanic polarization by an amount equal to $\tfrac{1}{2}\mathrm{CV}^2$, where C is the electric capacity of the surface per unit area.

The polarization-charge is therefore zero when T is a maximum, and the surface is then most curved.

The method that we have employed to determine the capil-

lary effect of the polarization-charge is different from that used by Lippmann and by Helmholtz. In their mode of procedure the variation of the energy of the system is expressed in terms of the variations of the surface-area and the surface-density, and it is claimed that this expression is an exact differential, *i. e.* that any series of operations whereby the area or density, or both, are changed so as finally to come back to the original values, will also bring back the energy of the system to its original value. This assumption seems to require justification when it is remembered how complex such a series of changes really is, and what a number of other variations besides those of volume and density may enter into it. Helmholtz appeals to Lippmann's experiments on the influence of extension of the surface-film on its electrification and *vice versâ*, and to his capillary engine, as pointing in a general way to the truth of the assumption.

In the method adopted above, we have proved the general theorem that the mechanical action of two layers of positive and negative electricity of equal amounts, spread over the two faces of a flexible sheet, may be represented by a negative surface-tension of amount numerically measured by the energy of the electrification per unit area. It follows, then, on this representation of the phenomenon, that no matter what other changes are taking place, the effect of the existing surface-charges is to diminish the surface-tension of the sheet by the amount just mentioned.

The case contemplated in the present application of this general proposition is that of a sheet of uniform thickness ; but we can clearly extend the result to flexible condensers of variable thickness of dielectric, provided always that the thickness be small compared with any radius of curvature of the surface at the place considered. In this case the mechanical effect on the condenser of a charge to potential V is to produce a negative surface-tension, numerically equal to $KV^2/8\pi t$, K being the dielectric constant and t the thickness of the sheet ; this surface-tension varies from point to point of the sheet, and is at any place inversely proportional to its thickness.

This result may also be at once deduced from the expression for the stress transverse to the lines of force in the dielectric on Maxwell's well-known theory.

4. Lippmann's original form of capillary electrometer consists of two mercury electrodes in contact with acidulated water. One of the electrodes is in an extremely fine capillary glass tube, so that the surface of contact is very small ; and the other is of considerable area. It follows that when a battery is applied, all the polarization and consequent change

in the surface-tension practically takes place at the fine electrode, as the corresponding charge at the other electrode is spread over so much greater area. The change in the capillary constant is measured by the column of mercury whose pressure is required to restore the meniscus to its former position.

Lippmann has given a series of observations with this instrument in his paper in the *Annales de Chimie,* vol. v. p. 507, the electrolyte being water containing one sixth part by volume of sulphuric acid. He finds that the maximum surface-tension is attained when the applied electromotive force is ·905 of a Daniell's cell. This value, therefore, corresponds to absence of polarization at the electrode meniscus. The following Table, calculated from his results, gives δe the excess (positive or negative) of the electromotive force above this value, δp the excess of the pressure required to neutralize its effect over its value when $e = ·905$ D, and $(\delta e)^2/\delta p$, which is proportional to the capacity of the electrode, and therefore inversely to the distance between the two electrified layers,—on the supposition that the condensing arrangement remains analogous to an ordinary condenser, viz. consists of two infinitely thin layers separated by a dielectric sheet.

$\delta e.$	$\delta p.$	$\dfrac{(\delta e)^2}{\delta p} \propto.$
$- ·89$ D	$343\frac{1}{2}$	23·07
$- ·88$	337	23·0
$- ·86$	$318\frac{1}{2}$	23·07
$- ·805$	$269\frac{1}{2}$	23·4
$- ·76$	$247\frac{1}{2}$	23·3
$- ·71$	$210\frac{1}{2}$	24·0
$- ·63$	170	23·3
$- ·54$	$123\frac{1}{2}$	23·6
$- ·405$	70	23·26
$- ·32$	$44\frac{1}{2}$	23·01
$- ·07$	2	24·05
$+ ·35$	$57\frac{1}{2}$	21·3
$+ ·43$	$79\frac{1}{2}$	23·3
$+ ·54$	$119\frac{1}{2}$	24·4
$+ ·81$	$230\frac{1}{2}$	28·5
$+ ·93$	$248\frac{1}{2}$	34·8
$+ ·98$	$254\frac{1}{2}$	34·2
$+1·10$	$264\frac{1}{2}$	45·8

The pressure supported by the tension of the meniscus when $e = ·905$ D was $1108\frac{1}{2}$ millim. of mercury, which is therefore proportional to the maximum surface-tension of the film. The surface-tension, as ordinarily measured, corresponds to $e = 0$, and is therefore proportional to the pressure, which was then 750 millim.

The last column of this table is in good agreement with Helmholtz's result, that for electromotive forces from zero up

to a limit of considerable magnitude the capacity of the con-
densing arrangement remains constant.

As δp is measured from a minimum value, it follows that in
the immediate neighbourhood of that value $(\delta e)^2$ *must* vary as
δp ; so that the discrepancies for small values of δp in the third
column are merely to be attributed to the special difficulty of
the observations in that part of the series.

Taking the second line of the table to give the average
value of this constant, we may calculate the thickness of the
dielectric, supposed to have the properties of vacuum, and
therefore to have unit specific inductive capacity, on the sup-
position that the arrangement acts as an ordinary condenser.
When $e=0$, Lippmann found by direct measurement that the
surface-tension was $\cdot 304 \times 981$ C.G.S. units, which there-
fore corresponds to $p=750$ millim. When $e=\cdot 024$ D, we
have $\delta e=-\cdot 88$, $\delta p=337$; therefore the change of the surface-
tension corresponding to δe is

$$\delta T = \frac{337}{750} \times \cdot 304 \times 981.$$

This, as we have seen, is equal to the energy of the polariza-
tion charge per unit area. Now, taking a Daniell to be $1\cdot 1$
volts, *i. e.* $1\cdot 1 \times 10^8$ C.G.S. electromagnetic units, which is the
same as $1\cdot 1 \times 10^8 \div (2\cdot 98 \times 10^{10})$ C.G.S. electrostatic units of
potential, we have,

$$\delta T = \frac{(\delta e)^2}{8\pi . \text{ thickness}} ;$$

therefore thickness of dielectric

$$= \frac{(\delta e)^2}{8\pi . \delta T},$$

$$= \left(\frac{1\cdot 1 \times \cdot 88}{298}\right)^2 \div \left(8\pi . \frac{337}{750} \times \cdot 304 \times 981\right),$$

$$= \frac{(\cdot 00325)^2}{3370},$$

$$= \cdot 313 \times 10^{-10} \text{ metre.}$$

This calculation has already been made by Lippmann
(*Comptes Rendus*, 1882, quoted in Thomson and Tait's
'Natural Philosophy,' 2nd edit., Appendix, "On Size of
Atoms "). It gives an estimate of a molecular distance, viz.
that at which the two electrified layers are held by molecular
chemical forces, which, notwithstanding the very rough sup-
positions on which it is founded, ought to be of the true order
of magnitude ; and Lippmann has pointed out that it agrees
sufficiently with the estimates assigned by Sir W. Thomson
and others from different considerations.

It is a satisfactory verification of the general notions in-

volved in this discussion to find that, notwithstanding the large factors occurring in the calculation, such as the ratio of the electrostatic and electro-magnetic units, it yet agrees so closely in order of magnitude with the result 1×10^{-10} metre, obtained by Helmholtz from actual measurement of the polarization capacity of platinum plates.

5. But, on the principles we have been following, we may carry the analysis of the phenomenon still further. The polarization consists in the transfer of charged particles towards the electrode under the action of the electromotive force, and they are finally brought to equilibrium at a distance from the electrode, whose order of magnitude has just been determined. As these equally charged particles repel one another, they will tend to settle down in equidistant positions along the electrode surface. Instead therefore of two electrified sheets analogous to an ordinary condenser, we have really two sheets, one consisting of equidistant electrified particles, and the other of the charges brought opposite to them on the electrode by induction. Each charged particle and its corresponding induced charge will be brought by their mutual attraction so close together that this attraction will just be balanced by the chemical forces which hold them apart.

For polarizations of sufficiently small amount, the sidelong action of the neighbouring particles will be so small as to have no appreciable effect on the distance of any one particle from the electrode surface ; because, in the first place, the distances of neighbouring particles must be at first large compared with the distance of two opposed charges, and, in the second place, the smaller forces exerted by these neighbouring particles must be resolved along the normal to the surface, in which direction they have no appreciable component. The radii of curvature of the surfaces are of course extremely great compared with the distance between opposed charges.

It follows that as the polarization is increased the number of charged particles over unit area of electrode increases in the same proportion, and these particles all come to rest at the same distance from the electrode surface, whatever be the amount of the polarization. And we can clearly expect this uniformity of distance to hold good until the neighbouring particles come within a distance of one another which is of the *same order* as the distance of a pair of the opposed charges.

The pair of opposed surfaces which is thus arrived at, not uniformly charged, but each with a system of equal isolated point-charges arranged uniformly all over it, does not, of course, act as an ordinary condenser in the sense of producing a constant fall of potential in crossing it at all points, in positions whose distances from it are of the same order as

the distance between neighbouring particles. But when we compare two points on opposite sides at distances from it great compared with this latter distance, it is immaterial whether the distribution is supposed to be in isolated points or uniformly spread over the surfaces. Therefore, as regards points not in the immediate molecular neighbourhood of the electrode, the effect of this polarization is still to produce simply a difference of potential on the two sides, which is just the same as if the charges were uniformly spread over the surfaces at the actual distance apart.

These considerations, then, give a reason for the fact which is brought out by the table given above, deduced from Lippmann's experiments with the capillary electrometer, and also independently by Helmholtz from direct measurement of the capacity of platinum electrodes in fluid with no dissolved gas (which would disturb the action); viz. that the polarization capacity is constant for all values of the applied electromotive force up to limits of considerable magnitude.

6. In order to form an estimate of the nearness of the neighbouring molecules on a face of the double sheet when they begin to exert an influence on one another comparable with that exerted by the opposite charges, we must assign a limit to the interval of potentials within which the capacity remains constant. The table in § 4 shows that we shall attain the correct order of magnitude by taking it to be, say, 1 volt in the case there considered.

We may now make the following calculation, bearing in mind that the sign = is to be interpreted as meaning that the quantities are of the same order of magnitude.

Let t be the thickness of dielectric layer ;

$\quad\quad$ d the distance between neighbouring atoms when their effective mutual action becomes comparable to that between opposed atoms (the important part of this action being that between any atom and the neighbours of its opposed charge) ;

$\quad\quad$ t' the mean molecular distance in the electrolyte ;

$\quad\quad$ e the constant aggregate charge of a single atom or radical ;

so that

$\quad$ $t'^{-3}e =$ the electro-chemical equivalent of 1 cubic centim. of water,

$$= \frac{10^5}{9} \text{ coulombs, approximately,}$$

$$= \frac{10^5}{9} \times 3 \cdot 10^9 \text{ electrostatic C.G.S. units,}$$

and $d^{-2}e =$ surface density.

We have, then, for the condensing sheet,

$$d^{-2} = \frac{V}{4\pi t},$$

where $V = 1$ volt,

$$= 10^8 \div (3 \times 10^{10}) \text{ electrostatic C. G. S. units.}$$

Therefore

$$\frac{1}{3} \cdot 10^{14} t'^3 d^{-2} = \frac{1}{3 \cdot 10^2 \cdot 4\pi t} \ ;$$

therefore

$$t'^3 d^{-2} t = \frac{1}{12} \cdot 10^{-16}.$$

If now we write for t the value found above, $\cdot 3 \times 10^{-8}$, and put t' and d equal to each other, both being molecular distances of the same kind, we obtain for either the value

$$\frac{4}{15} \times 10^{-8} \text{ centimetres,}$$

which is very exactly of the same order as the value for molecular intervals obtained already from the other considerations.

On looking through this calculation it will be seen that quantities which we have designated as of the same order of magnitude do not differ nearly so much as in the ratio ten to one.

7. The two estimates of molecular distance which have thus been found on independent considerations connected with galvanic polarization therefore agree within very close limits; and they come very close to the third value determined by Helmholtz on the same theory of galvanic polarization, viz. 1×10^{-8} centim.; and they are also just below the superior limit assigned by Sir W. Thomson to molecular intervals from various considerations connected with different physical phenomena, viz. 10^{-8} centim., his inferior limit being $\frac{1}{20} \times 10^{-8}$ centim.

Sir W. Thomson's different arguments lead to the following superior and inferior limits of the average distance of molecules from one another in solid and liquid substances :—

	centim.	centim.
Contact electricity	1×10^{-8}	$\frac{1}{4} \times 10^{-8}$
Surface-tension	$\frac{1}{2} \times 10^{-8}$	
Kinetic theory of gases		$\frac{1}{5} \times 10^{-8}$
Solids and liquids	$\frac{7}{10} \times 10^{-8}$	$\frac{1}{5} \times 10^{-8}$

to which we may now add

Helmholtz . . . . 1×10^{-8};

while Lippmann's method places the mean at $\frac{3}{10} \times 10^{-8}$ centim.; and the other method here given places it at $\frac{4}{15} \times 10^{-8}$ centim., with as small limits of error as any of the methods given above.

8. The chief value of this discussion seems, however, to be not so much that it gives an estimate of molecular distance, but that its very close agreement with the other independent estimates derived from considerations connected with the same phenomenon of galvanic polarization is strong evidence of the substantial and ultimate truth of that representation of the phenomenon which has formed the basis of the discussion.

This argument seems to derive very great weight from the wide variety and very different magnitudes of the physical constants employed in the three calculations, one depending on the direct measurement of the polarizing charge, another on the direct measurement of change in the capillary constant, and the third involving, in addition, the knowledge of the quantity of electricity required to decompose a gramme of water; while they all involve in different ways a constant of such large numerical magnitude as the ratio of the two electrical units of quantity.

9. The critical value ·905 D in § 4 appears to have an important bearing on the much discussed question of contact electrification.

As was pointed out by Helmholtz, a discontinuous change of potential in crossing a surface can only be produced by the existence of an electrical double layer on that surface; so long as we look upon electrification or electric distribution as the cause of electrical phenomena, this is the only explanation open to us.

It has been seen that this electrification represents a distribution of purely surface-energy; and if its properties are to

be investigated, it is to be expected that much light will be thrown upon them by their relations to other purely surface-distributions of energy, of which the best known is that leading to capillary phenomena.

We are not required to explain the manner in which this double layer at the surface of contact of two dissimilar substances is brought about. We may illustrate it by the rather crude hypothesis that each molecule of an electrolyte consists of a positively charged cation radical and a negatively charged anion radical held together by electrical forces, but partly also by their forces of chemical affinity, so as to be analogous to a magnetic molecule with north and south poles; that along the surface of the electrode these molecules are all turned into the same direction (polarized) by reason of the greater chemical affinity of one of their constituents for the matter of the electrode; and that they thus form a double sheet analogous to a magnetic shell. This illustration will at any rate show that it is possible to give an account of the matter which shall be in unison with the commonly received ideas of electrical and chemical action, without having to speculate on the deeper question of the relation of the material atom to its electrical charge.

The electro-capillary observations of Lippmann quoted above, and the later ones of Koenig for various electrolytic fluids, show that, for one definite amount of polarization, each of these fluids in contact with mercury shows a maximum surface-tension. As we have seen that the existence of an electrical double layer on the surface must diminish the surface-tension, it follows that the critical value ·905 D for Lippmann's acidulated water is that difference of potential which, applied from without, just neutralizes the naturally existing double electrical layer on the surface. It would seem therefore that the natural contact-difference of potential between Lippmann's mercury and acidulated water is ·905 D, and that an absolute measure of a contact electromotive force has thus been obtained.

Appendix.

The result that the mechanical effect of the electrification on a charged condenser with thin uniform dielectric, whether flexible or not, is equivalent to a uniform negative surface-tension, has been derived in § 2 from the Principle of Energy without the use of any analysis.

The same result will of course follow from direct calculation of the mutual forces exerted by the charged elements of the surfaces on one another. As it forms a good example of the

theory of surface-energy which Gauss has made the founda-
tion of the doctrine of capillary action, in a case in which all
the circumstances of the forces are known, and as it also
illustrates some other points, the direct calculation is here
appended.

Consider, first, an infinite plane electrified surface, and
imagine a straight line drawn across it. The mutual repulsion
of the electrified parts on the two sides of this line will result
in a tension tending to tear the parts of the surface asunder
along the line, and whose intensity, measured across unit length,
we can calculate as follows.

Imagine a unit of electricity situated at a point distant ξ
from the line of division; the repulsion exerted on it by the
other half of the electrification is easily expressed in polar
coordinates, r, θ; θ being measured from the shortest distance
to the line of separation.

It will, however, be more convenient to take this unit charge
at a distance h from the plane, and to measure r, θ from its
projection on the plane as pole. The repulsion exerted on it,
resolved parallel to the plane, is

$$2\int_\xi^\infty dr \int_0^\phi d\theta r \frac{r}{(h^2+r^2)^{\frac{1}{2}}} \cdot \frac{\rho\cos\theta}{h^2+r^2},$$

where ρ is the surface-density of the electrification, and
$\cos\phi = \xi/r$.

Therefore the repulsion

$$=2\rho\int_\xi^\infty dr \frac{r(r^2-\xi^2)^{\frac{1}{2}}}{(r^2+h^2)^{\frac{3}{2}}}.$$

To integrate this, write

$$r^2-\xi^2 = (r^2+h^2)z^2;$$

therefore

$$rdr = \frac{r^2+h^2}{1-z^2}zdz;$$

and the integral

$$=\int_0^1 \frac{z^2}{1-z^2}dz$$

$$=\left[\tfrac{1}{2}\log\frac{1+z}{1-z}-z\right]_{z=0}^{z=1}.$$

This quantity becomes infinite at the upper limit; so that
for an infinite plane sheet the tearing-force due to the electri-
fication would be infinite; a result which would also follow
readily from simple consideration of the dimensions of the
variable involved in the integral.

Suppose, however, we take a finite sheet bounded on the

further side by the circular arc $r = r_0$; the repulsion now is

$$\mathrm{R} \equiv 2\rho \log \{ (r^2_0 + h^2)^{\frac{1}{2}} + (r^2_0 - \xi^2)^{\frac{1}{2}} \} - \rho \log (h^2 + \xi^2)$$
$$- 2\rho \left(\frac{r^2_0 - \xi^2}{r^2_0 + h^2} \right)^{\frac{1}{2}}.$$

As we have seen, this expression increases indefinitely as r_0 increases. But if now, instead of a single electrical sheet, we had a double electrical layer with an intervening vacuum dielectric of thickness t, the repulsion exerted by it on the unit charge in the plane of the positive face will be equal to

$$t \frac{d\mathrm{R}}{dh}.$$

But on differentiating the expression for R, it is obvious that the first and last terms give parts which become zero when r_0 is infinite ; so that the repulsion of the infinite double layer on the unit charge is finite, and is equal to

$$\frac{2t\rho h}{h^2 + \xi^2}.$$

The repulsion exerted on a strip of unit breadth of density ρ and extending from $\xi = 0$ to $\xi = \infty$ therefore

$$= \rho \int_0^\infty \frac{2t\rho h}{h^2 + \xi^2} \, d\xi$$
$$= \pi\rho^2 t,$$

which is independent of h.

The repulsion exerted on a strip of the same *double* sheet is therefore

$$2\pi\rho^2 t,$$

i. e. it is the electrical energy of the distribution per unit area. And this quantity that we have thus calculated is clearly the surface-tension required.

It is clear also that the stress across any line drawn on the sheet is wholly tangential, and has no component normal to the sheet; so that this surface-tension is its complete specification.

The calculation just made has been only for the case of an infinite plane double sheet. For a single sheet the distant parts exert a finite effect; and we have seen that the stress increases indefinitely when the size of the sheet increases. But for a double sheet the parts very distant relatively to the thickness no longer contribute sensibly to the result, and the integrals converge. Thus, if the double sheet be of sensible but finite curvature, we may calculate the integrals either

from the sheet itself or from the portion of the sheet which coincides sensibly with the tangent plane at the place considered, or from an infinite plane sheet coinciding with that tangent plane. This is on the assumption that the part of the sheet which coincides sensibly with the tangent plane is of large dimensions compared with the thickness of the dielectric, *i. e.* that the latter is small compared with any radius of curvature of the sheet.

The result obtained therefore holds for curved double sheets as well as plane ones.

Now, if a curved sheet be under a uniform surface-tension T, it is well known that the stress experienced by any element δS of its surface is along the normal, and equal to

$$\text{T}\left(\frac{1}{\text{R}_1} + \frac{1}{\text{R}_2}\right)\delta\text{S},$$

R_1, R_2 being the principal radii of curvature where δS is situated. When we apply this to the electrical double layer, we obtain the same result as comes from the direct expression, on Green's theory, of the force exerted by the electrical system on the two charged faces which belong to the element δS.

For a single curved electrified layer of finite dimensions, open or closed, the surface-tension is different at different points, and at the same point across different lines on the surface; except in the case of an electrified spherical sheet, in which it is easily seen to be constant and equal to $-\pi\rho^2 a$, where a is the radius of the sphere.

September 11, 1885.

L. *On the Influence of Pressure on certain cases of Electrical Conduction and Decomposition.* By J. W. CLARK, *Assistant Professor of Physics in University College, Liverpool*[*].

AS the subject of electrolysis is to be brought prominently before the next Meeting of the British Association, the following short outline of an investigation, commenced some years ago, may not be without interest at the present time.

The subject properly divides itself into three branches, viz.:—the influence of pressure on the electrical conduction and decomposition of—

I. Dilute sulphuric acid (products of electrolysis occupying much greater volume than when combined to form the electrolyte).

II. A solution of (*e. g.*) $CuSO_4$ (products of electrolysis

occupying about the same volume as when combined to form the electrolyte).

III. The conduction of mercury.

Of these three classes, it will be noticed that the liquids in I. and II. are composed of complex molecules which, according to Clausius, are in a state of continuous motion varied by collisions with one another which cause dissociation[*].   Mercury, on the other hand, is a metallic conductor, and a liquid which is usually regarded as being composed of simple or monatomic molecules, which are therefore incapable of undergoing dissociation ; but by the application of a sufficient external pressure its molecules may be brought nearer together, or, in other words, the lengths of the molecular mean free paths may be reduced.

The investigation to which I now wish to refer relates to the decomposition of dilute sulphuric acid under an external pressure which it is my object to make appreciable in comparison with the molecular forces of the liquid itself, for it is only when that condition is fulfilled that any direct results are to be anticipated such as those which are here sufficiently suggested by the questions :—Is Faraday's law independent of pressure ? Do the conduction and decomposition of an electrolyte always vary together? Can electrolytic action be stopped by pressure ?   It was to obtain a reply to such questions that I turned from the region of speculation to the surer ground of experiment, and in the first instance set myself to measure the electrical resistance of acidulated water, and the amount of gas liberated from it by a known current under pressure.

The method of experiment in outline is as follows :—The dilute sulphuric acid to be electrolyzed is hermetically sealed in a short glass tube (0·1 centim. in internal, and 0·7 centim. in external diameter), through the ends of which pass thin platinum-wire electrodes, of which the upper wire is usually so encased in glass that only the portion in the electrolyte is exposed : a precaution found to be necessary in order to avoid continuous recombination.   This roughly describes the " *electrolytic tube*," in which the pressure upon the dilute sulphuric acid is generated by the gases liberated by the current as they accumulate in the (determined) volume of the tube which is unoccupied by the liquid.   When the circuit includes a gal-

---

[*] If volatility and a large coefficient of expansion for heat may be regarded as a probable indication of a long mean free molecular path, it does not seem impossible, on the hypothesis of Clausius, that under the influence of a sufficiently great external pressure, such liquids as condensed gases (CO_2, NH_3, SO_2, &c., fused $HgCl_2$), might be rendered good electrical conductors, or at least have their conductivity increased.

vanometer as well as a silver voltameter, variations of current, as well as total current, can be measured ; and, finally, the quantity of gas liberated in the electrolytic tube under the accumulating pressure exerted by it upon the liquid is determined by allowing it to burst in a stoppered eudiometer (of special construction) over mercury, so that the whole of the gas is collected. From the volume of gas thus obtained the bursting or maximum pressure can be calculated.

The principal results may be very briefly stated as follows:—

1. When such an electrolytic tube containing dilute sulphuric acid is fixed in a vertical position, the lower electrode connected with the positive and the upper electrode with the negative pole of a battery, the evolution of gas appears to become less and less, and the electrical resistance of the contents of the tube increases, until, with an E.M.F. of 30 volts, the needle of a galvanometer in circuit shows only a very small deflection. This action appears to be due to the formation of very dense sulphuric acid (H_2SO_4 ?) at the + electrode at the bottom of the tube, whilst the water from which it has been separated forms a layer above it of so high resistance as to almost absolutely stop the passage of the current. This condition must not be mistaken for the cessation of electrolytic decomposition produced by pressure.

The strong acid is produced at the + electrode by the action of the current, and owing to the small sectional area of the tube, though it again mixes with the liquid above it by diffusion, it does so less rapidly than it is separated by the current. Moreover, under a sufficient pressure diffusive rate is lessened as the length of the mean free molecular path is decreased.

The above singular action affords a means of concentrating sulphuric acid without boiling.

2. When the poles are reversed, the dense sulphuric acid is formed by the current at the upper electrode, and thus becomes again mixed with the rest of the liquid in the tube as it descends through the liquid, the mixing action being facilitated by the bubbles of hydrogen rising from the lower electrode. In this way the separating action of the current is prevented, and my glass tubes (which burst at about 290 to 300 atmospheres) fail to withstand the pressure of the gases liberated by the current. I sought to strengthen one glass tube of special form by first coating it with pure silver by Martin's method, and then thickly electrotyping it with copper ; but it also burst. It is certain, therefore, that a pressure of 300 atmospheres is insufficient to arrest the electrolytic decomposition of dilute sulphuric acid. I am not yet certain whether pressure exercises any direct influence on the

electrical resistance and on the quantity of gas liberated from dilute sulphuric acid, but what there is is slight. There seems to be a small decrease in the resistance, but I cannot yet say to what this is due ; for this part of the investigation is incomplete, and it is exceedingly difficult to distinguish and separate between possible causes.

3. Ozone is present in the gases liberated by the bursting of the electrolytic tube. 1 have not estimated it quantitatively, but I have no reason to think it present in unusual amount. Under some conditions, *e. g.* during the formation of ozone under the influence of the silent discharge, pressure might facilitate the condensation of oxygen to ozone.

It may, finally, be needful to increase the pressures employed in this investigation still more, and to employ vessels of steel or of some other material. The whole investigation is one of great difficulty, but I shall probably publish a fuller account of the methods and results of which the above forms a short and very imperfect summary*.

Addenda to the Author's paper " On certain Cases of Electrolytic Decomposition," Phil. Mag. July 1885.

Page 38, line 5 from top, *omit* binary.

Page 38, *add*:—Dr. Gore has discovered that heated argentic fluoride commences to conduct while still solid, and that when fused its electrical resistance is very small. He appears to regard the conduction in both cases as being unaccompanied by decomposition, *i. e.* non-electrolytic.

Page 43, line 15 from top, *for* (and Hg_4I_6) *read* (and HgI_6?).

Page 39, line 6 from bottom, *add* :—It is of interest to remark, in connection with the electrolytic decomposition of glass at 100° C., that I have recently learnt from Mr. Hicks that it may also be annealed at this temperature.

Pages 40 and 45, *add* :—Amongst the properties of fused

---

* To the proof I have an opportunity of adding that, since the above was written, I have found a short paper by M. Bouvel in the *Comptes Rendus*, t. lxxxvii. p. 1068, wherein he states that he has found experimentally that :—

(1) La décomposition de l'eau par un courant est indépendent de la pression.

(2) La quantité de l'électricité nécessaire pour décomposer un même poids d'eau est sensiblement la même quelle que soit la pression à laquelle s'opère la décomposition.

M. Bouvel verified these statements up to 200, and found that the decomposition was not stopped by a pressure of 360 atmospheres.

mercuric iodide and chloride which led me to infer that the
molecules of these substances may possess an unusually long
mean free path of liquids, I omitted to mention their large
coefficients of expansion for heat.

August 8, 1885.

LI. *On the Winters of Great Britain and Ireland, as influenced
by the Gulf-Stream. By* Prof. HENRY HENNESSY, *F.R.S.**

IN the ninth volume of the Proceedings of the Royal
Society, p. 324, is printed a letter which I wrote to the
late General Sir Edward Sabine, on the influence of the Gulf-
stream on the winters of the British Islands. I pointed out
that if abnormally cold or warm winters are due to changes
in the condition of the comparatively tepid currents bathing
our shores, then during cold winters the differences of tempe-
rature between the Northern and remaining coasts should be
greater than during mild winters. A comparison of the
observations made in the months of December 1855, 1856,
and 1857 presented precisely this result. The winters of
some recent years having exhibited abnormal features as to
temperature, I have made a comparison of the results pub-
lished by the Meteorological Office, of which the following
may be taken as the leading facts.

In comparing the coast-temperatures of Great Britain, it
should be remarked that the island is shaped in an irregular
triangular outline, of which the summit is in North Scotland,
and the base the south coast of England. For temperature-
comparisons it is therefore best to compare the South coast
with the West coast and North-east coast.

In the winters of 1871 and 1881 the month of January was
cold in Great Britain, and the following results have been
grouped as indicated :—

1871. (Cold.)

SOUTH COAST.	WEST COAST.	NORTH-EAST COAST.
Helston ...... 41·1	Barnstaple .... 37·0	Holkham .... 32·2
Truro.. ...... 38·9	Llandudno .... 36·1	Boston ...... 31·6
Sidmouth .... 36·6	Liverpool .... 33·5	Hull .... 31·3
Eastbourne.... 35·2	Cockermouth .. 33·7	Whitby .... 31·6
Ventnor ...... 36·8	Silloth ...... 33·0	Shields ...... 33·0
Osborne ...... 35·0		
Bournemouth.. 35·1		
Worthing .... 34·9		
Mean .... 36·7	Mean .... 34·7	Mean .... 31·9

Excess of South over West coast.......... 2·0
Excess of South over North-East coast .... 4·8

Communicated by the Author.
2 I 2

1881.   (Cold.)

South Coast.		West Coast.		North-East Coast.	
Dover	35·0	Pembroke	36·0	Yarmouth ..	32·5
Hastings... ..	35·2	Holyhead	36·4	Gelderston ..	31·7
Southampton..	33·4	Llandudno	34·9	Spurn Head ..	33·2
Hurst Castle ..	34·6	Douglas	33·2	Shields	30·9
Plymouth	35·6	Liverpool	31·5	Leith	29·9
Falmouth	38·5	Silloth	27·5	Aberdeen	28·5
Prawle Point..	37·1	Barrow	32·3	Nairn	28·6
		Laudale	31·5	Alnwick	28·6
		Ardrossan	31·6		
Mean	35·6	Mean	32·8	Mean	30·5

Excess of South coast over West coast ...... 2·8
Excess of South coast over North-East coast .. 5·1

For Ireland, the following results have been obtained for January 1881.   (Cold.)

North Coast.		South Coast.	
Mullaghmore	35·2	Roches Point	37·0
Londonderry	30·9	Valentia	39·0
Donaghadee	35·2		
Mean	33·8	Mean	38·0

Difference .... 4°·2

In 1883 the three weeks ending December 31 were *warm*, and the following were obtained for Great Britain :—

South Coast.		West Coast.		North-East Coast.	
Dover	41·6	Pembroke	45·4	Sumburgh Head	42·5
Hastings......	41·8	Holyhead	45·4	Stornoway	41·0
Southampton..	41·9	Llandudno	45·0	Wick	39·4
Hurst Castle ..	42·8	Liverpool	43·1	Nairn	41·3
Plymouth	43·9	Barrow	42·7	Aberdeen	39·2
Falmouth	45·2	Silloth	41·6	Leith..........	42·7
Prawle Point..	43·8	Ardrossan	43·2	Alnwick	41·2
		Laudale	42·7	Shields	41·5
				Scarborough ..	41·5
				Spurn Head	40·4
				Yarmouth......	40·0
				Gelderston	40·4
Mean	43·0	Mean	43·6	Mean	40·9

Excess of South coast over North-East coast .... 2·1
Defect of South coast compared to West coast .. −0·6
Excess of South over all the rest .... 1·0

During the same month (December 1883) the following results were obtained in Ireland :—

NORTH COAST.		SOUTH COAST.	
Londonderry	43·9	Roches Point	45·3
Mullaghmore	44·6	Valentia	46·7
Donaghadee	43·1		
Mean	43·9	Mean	46·0

Excess of South over North coast...... 2°·1

The mean temperature at Dublin was 43°·6 ; whence, if this may be taken as about the temperature of the East coast, the North exceeded the East by 0·3.

If we now compare the cold and warm periods, we observe that both in Great Britain and Ireland the difference between the Southern and Northern coasts was less in the warm period than in the cold ; and the influence of warm currents was also exhibited in the higher temperature of northern over eastern stations at lower latitudes. The conclusion arrived at in my former comparisons has been thus supported, and the influence of the thermal currents surrounding these islands in modifying the winters appears to be further confirmed.

In a paper of General Sabine's, to which I have referred in the communication printed in the Proceedings of the Royal Society, he mentioned the winter of 1845–46 as exceptionally mild. Some confirmation of the law I indicated may be derived from some observations made during that winter on the south-west coast of Ireland by Mr. Daniel O'Connell. The results were communicated by the son of the illustrious orator to the late Dr. Humphry Lloyd; and having consulted the record, I found that Mr. O'Connell observed the temperature daily at Darrynane Abbey for 106 days during the winter of 1845–46, from November to February ; on applying the corrections recommended by Dr. Lloyd in his paper on the Meteorology of Ireland, I found that the mean for the winter at Darrynane Abbey was 47°. During the four winter months referred to, the mean temperatures were as follows at other stations :—

Cork	47·5
Dublin	46·3
Swansea	44·4
St. Heliers (Jersey).	46·4
Orkney	41·8

The winter of 1845–46 seems therefore to furnish an illustration of the law of temperature-distribution already mentioned, and therefore of the influence of the heat-bearing currents which wash the shores of these islands.

LII. *On the Comparative Temperature of the Northern and Southern Hemispheres of the Earth. By* Prof. HENRY HENNESSY, *F.R.S.**

MORE than twenty years have elapsed since I published a systematic proof of the superiority of water over land as a substance for absorbing and gradually diffusing throughout its mass the heat received from the sun. The superficial portions of the earth as a whole, including the atmosphere in contact with the water, would be thus influenced, and in this way the physical properties of water were shown to have a predominant influence on terrestrial climate.

The properties of water here referred to are :—(1) Its exceptionally high specific heat ; (2) its moderate permeability to luminous rays of heat contrasted with its impermeability to obscure heat ; and (3) its mobility. From Pfaundler's observations and experiments it appears that the specific heat of the soil, which forms the general surface of dry land exposed to the atmosphere, to sunshine and planetary space radiation, varies from 0·19 up to 0·5. The majority of soils have specific heat of from 0·25 to 0·28. Thus the absorbing-power of dry land for radiant heat is in all cases much less than that of water. At night land more readily parts with the heat acquired under sunshine, and from its immobility it cannot directly transport by convection or by currents any of the heat it acquires to other parts of the earth's surface. The conclusions at which I arrived were entirely different from those which were generally received anterior to the time of the publication of my views. The generally received notions at that time are best summed up in the words of Sir John Herschel :—"The effect of land under sunshine is to throw heat into the general atmosphere, and to distribute it by the carrying-power of the air over the whole earth. Water is much less effective in this respect, the heat penetrating its depth and being there absorbed, so that the surface never acquires a very elevated temperature." †

These words occur in the latest edition of the work from which they are quoted. They furnished Sir Charles Lyell the groundwork of some of his ingenious reasonings regarding Geological Climate ; but my conclusions were so different that they might be fitly expressed in terms diametrically

* Translated, with additions, from the *Comptes Rendus* of the **Paris** Academy of Sciences for September 1882.

† ' Outlines of Astronomy.'

opposite, and in such terms I have in fact expressed them long since as follows :—The effect of land under sunshine is to rapidly throw off the heat it receives into the upper regions of the atmosphere and the interplanetary spaces both by day and by night ; and thus, although it causes a considerable increase of temperature in the strata of air over it by day, it is not well adapted for storing up and retaining heat. Water is much more effective in this respect ; the heat penetrates to a greater depth within it than on dry land, and it becomes more completely absorbed, owing to the far higher capacity for heat of water and the difference between its diathermanous action on the luminous heat-rays entering it from the sun compared with its action on the obscure rays quitting the particles in the interior of its mass.

Among the consequences following from my theory of terrestrial climate was one which seemed difficult to reconcile with the facts accumulated at the time this theory was brought forward. I refer to the supposed higher temperature of the northern as compared with the southern hemisphere. This was formerly attributed to the heating-power of the great masses of land north of the equator. I could not account for this inequality unless by supposing that oceanic and aerial currents which had not been as yet fully examined transported some of the heat absorbed south of the equator to its northern side. This supposed superiority of temperature in the northern hemisphere was employed as an argument against my conclusions.

In 1875, at the meeting of the British Association at Bristol, I brought forward my views for the purpose of establishing my priority in regard to some of the conclusions which had been frequently reproduced at different inquiries in Great Britain without any reference to their original source. In the discussion which followed one of the speakers, Prof. Everett, is reported to have asked, " How, assuming Professor Hennessy's theory without acknowledgment to be correct, it could be reconciled with the generally accepted fact that the temperature of the northern hemisphere was greater than that of the southern. Professor Hennessy denied that this was a fact, but supposing it were so, he would attribute it to oceanic currents."

It now appears that the notion of any superiority of mean temperature in the northern as compared to the southern hemisphere must be abandoned. When this opinion gained currency the number of temperature-observations made south of the equator was very small compared to the number recorded in northern latitudes. Of late years a considerable

number of observations on the temperature of the sea and air have been collected and published by the Government of the United States of America. From these observations the result has been deduced that the difference of temperature between the two hemispheres is insensible, and probably slightly in favour of the higher mean temperature of the hemisphere which possesses the largest water-covering*. In this way my theoretical views have been fully confirmed by the crucial test of leading to conclusions which did not seem likely to be true at the time I originally placed them on record.

Some further illustrations of the question under consideration may be obtained from the results of observations on the distribution of a well-known class of plants. The conditions most favourable to the growth of the larger ferns were recognized by Robert Brown and other eminent botanists to be humidity, shade, and uniformity of moderately elevated temperature. These conditions exist in their most perfect form among the smaller islands of the great oceans. In islands like New Zealand and others of inferior size the tribes of plants alluded to are widely spread and highly developed. The relative distribution of these plants in the northern and southern hemispheres is highly instructive. The extratropical regions of the northern hemisphere contain thirteen times as much land as the corresponding portion of the southern hemisphere, and in the latter arborescent ferns are known to grow much further from the equator than in the former.

Professor Lindley remarked long since that at the time of the deposit of the Lias formation, a geological epoch of somewhat higher general temperature than the present, the vegetation was similar to that of the southern hemisphere in the Pines as well as in the Cycads.

LIII. *On Retardation of Chemical Change.* By JOHN J. HOOD, *D.Sc. (Lond.), Assoc. Royal School of Mines*†.

IN a short paper published in this Journal‡ some time ago, on Retardation of Chemical Action, it was shown that

---

the rate at which ferrous-sulphate solution is oxidized by potassic chlorate is retarded in a remarkable manner by the addition of various sulphates. The principal results obtained were these—that the amount of such retardation is proportional to the quantity of the sulphate added, and that certain groups of analogous sulphates produce, for equal weights, the same retardation-effect. For instance, equal weights of the sulphates of sodium, potassium, and ammonium were found to produce the same amount of retardation ; so also did the potash- and ammonia-alums ; whereas the sulphates of zinc and magnesium, although classed together as analogous salts in the same sense as those of the alkali metals, produced different retardations. The natural inference that was drawn from these experiments was, that the study of retardation might afford a means of classifying chemical substances on a dynamical basis, and of determining for each salt or group of salts a numeric, the coefficient of retardation, of a character somewhat similar to what Mills* has termed the "bergmannic" of a salt. Owing to the small number of soluble sulphates that can be employed in the above reaction for studying their retardation-effects, it is very limited in its application ; consequently search was made for other reactions that could be employed for the same purpose, of such a nature that nitrates or chlorides could be experimented with. Of the several reactions that were tested for this purpose, it was found that the oxidation of ferrous chloride by potassic chlorate was by far the best, being analogous in all respects to that of the oxidation of ferrous sulphate, and capable of being rendered as quick or as slow, by alteration of conditions, as might be necessary for the purpose in view ; besides, the list of soluble chlorides whose retardation-effects could be studied is a comparatively large one. The results, however, that have been obtained with these salts are such as have modified somewhat the author's original notions concerning retardation and the molecular movements that are generally supposed to take place in a system undergoing chemical change.

It has been usual, in establishing the formulæ that are employed in the study of the rate of chemical change, to ignore the fact that the products of the reaction, however inactive they may be in the chemical sense, may retard the rate of the change considerably. In the experiments with ferrous sulphate referred to, it was shown that the introduction of so small a quantity as one gram of the sulphates of the alkali metals in 260 cubic centims., the volume of the experimental

* Phil. Mag. [5] i.

solution, caused the oxidation to progress at a rate 10 per cent.
less than when no such salt was added ; an effect which might
be produced even to a much greater extent by the products
gradually formed during the course of any chemical change,
especially where the quantities of material in unit volume are
comparatively large, as, for instance, in the many cases of
etherification that have been studied dynamically during the
last few years, and might consequently vitiate somewhat the
inferences drawn from such experiments.

As it was found in the experiments alluded to that the
amount of retardation was proportional to the amount of the
sulphate added, it would naturally be supposed that the pro-
ducts formed during a reaction would produce a retarding
or accelerating effect (for the latter is possible, as these
experiments show) proportional to their quantity ; and it is
easy on this hypothesis to introduce this effect into the
equations.

Suppose in a chemical system undergoing change there are
n different bodies taking part in the reactions, and the mea-
surements that are made of the progress of the change relate
to one of these n bodies.   Let $A_1, A_2, \ldots A_n$ be the initial
quantities of the active substances, and at time t from the
commencement of the change $\alpha_1, \alpha_2, \ldots \alpha_n$, the quantities of
these that have become chemically inactive members of the
system, and let the measurements that are made relate to the
body A_κ.   At time t the quantities of these substances that are
still capable of reacting one with the other will be $A_1 - \alpha_1$,
$A_2 - \alpha_2, \ldots A_n - \alpha_n$; and the inactive products resulting from
the changes that have taken place will be $\alpha_1 + \alpha_2 + \ldots \alpha_n$. Then,
on the usual hypothesis that the amount of change that takes
place in unit of time with regard to any one of these bodies,
A_κ, is proportional to the product of the active substances, and
that the retardation- or acceleration-effect of the products of
the reaction is proportional to their amount, the equation
representing this would be written

$$\frac{d\alpha_\kappa}{dt} = \mu \frac{(A_1 - \alpha_1)(A_2 - \alpha_2) \ldots (A_n - \alpha_n)}{B \pm (\lambda' \alpha_1 + \lambda'' \alpha_2 \ldots \lambda^n \alpha_n)}, \quad \cdot \quad \cdot \quad (1)$$

where λ', λ'', &c. are the coefficients of retardation *or accele-
ration* of α_1, α_2, &c., and $\pm$ is taken according as these
effects are all of the first or of the second character.   The
nature of the effect of each individual product α_1, α_2, &c.,
whether $\pm$, could be determined experimentally by adding a
considerable quantity, and noting the difference in the rate of

such an experiment and of one where no such substance is present excepting what is formed during the reaction.

If the initial quantities A_1, A_2, ... A_n are in equivalent proportions, they may be expressed in terms of A_κ, thus $A_1 = \epsilon_1 A_\kappa$ ... $A_n = \epsilon_n A_\kappa$. But suppose for the most general case that they are multiples of these quantities, or $A_1 = \nu_1 \epsilon_1 A_\kappa$ ... $A_n = \nu_n \epsilon_n A_\kappa$; α_1, α_2, ... α_n, however, are always in equivalent proportions, or $\alpha_1 = \epsilon_1 \alpha_\kappa$ ... $\alpha_n = \epsilon_n \alpha^\kappa$. Substituting these values, (1) becomes

$$\frac{d\alpha_\kappa}{dt} = \frac{\mu(\nu_1\epsilon_1 A_\kappa - \epsilon_1\alpha_\kappa) \ldots (A_\kappa - \alpha_\kappa) \ldots (\nu_n\epsilon_n A_\kappa - \epsilon_n\alpha_\kappa)}{B \pm \alpha_\kappa(\lambda_1\epsilon_1 + \lambda_2\epsilon_2 \ldots + \lambda_n\epsilon_n)}.$$

Writing $A_\kappa - \alpha_\kappa = y$, the amount of A_κ that remains active at time t, and $\dfrac{d\alpha_\kappa}{dt} = -\dfrac{dy}{dt}$. This equation may be written in the form

$$\frac{dy}{dt} = -\frac{ay\{(\nu_1-1)A+y\}\{(\nu_2-1)A+y\} \ldots \{(\nu_n-1)A+y\}}{b \mp y}. \quad (2)$$

The reaction under consideration (the oxidation of ferrous chloride by potassic chlorate) is represented by the equation

$$6\,FeCl_2 + KClO_3 + 6\,HCl = 3\,Fe_2Cl_6 + KCl + 3\,H_2O\;;$$
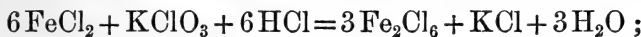
and consists of a system of three active members, in which the iron, or y, was made the subject of measurement. In the preliminary experiments that were made, the ratios of the chlorate and acid to the iron were varied, in order to find the quantities, and consequently the rate, of the oxidation most suitable for bringing out the retardation-effects of the chlorides. Some experiments were made with all three materials in equivalent quantities which would be represented by the equation

$$\frac{dy}{dt} = -\frac{ay^3}{b \mp y}.$$

But such conditions were unsuitable; for the experiments showed, as is evident from this equation, that, as the rate varies as the third power of y, at the start the reaction proceeds very rapidly, and quickly becomes very slow, a state of matters most inconvenient for the purpose in view. It was ultimately found best to employ different multiples of equivalents of acid and chlorate for the different purposes of studying retardation of sulphates, of chlorides, and influence of temperature, as given below.

The preliminary experiments with the chlorides showed

that these substances, even in large quantity, influenced the rate of the change comparatively little; and that consequently the term in (2) relating to the retarding or accelerating effects of the products of the reaction could be neglected; as indeed the calculations from the experimental numbers showed to be true, as is illustrated in the experiments with $MgSO_4$ given in detail below.

For part of the work relating to the retardation of sulphates and influence of heat, the following equation was employed:—

$$\frac{dy}{dt} = -ay\{(\nu_1-1)A+y\}\{(\nu_2-1)A+y\},$$

which, on integrating, gives

$$f\left\{(\nu_2-1)\log_{10}\frac{y+(\nu_1-1)A}{y} - (\nu_1-1)\log_{10}\frac{y+(\nu_2-1)A}{y}\right\} = g+t; \quad (3)$$

whilst in the experiments with chlorides the iron and chlorate were in equivalent quantities, and the acid several multiples, represented by the equation

$$\frac{dy}{dt} = -ay^2\{(\nu_2-1)A+y\},$$

which, on integrating, becomes

$$f'\left\{(\nu_1-1)A - \frac{y}{\cdot4343}\log_{10}\frac{y+(\nu_2-1)A}{y}\right\} = y(g'+t). \quad (4)$$

Taking either of these equations (3) and (4), it is easy to see that $\frac{dy}{dt} \propto f^{-1}$, or that the time required to oxidize the iron from y' to y'' is proportional to f; consequently in a series of experiments in which everything is the same excepting the presence of inactive salts, by a comparison of the values obtained for f with its value for an experiment in which no such extraneous salt is added, or a blank experiment, a measure is obtained of the effect of such a salt on the rate of the oxidation; so also in the case of variations of temperature a measure is obtained of the accelerating effect of heat on the rate.

Sulphates.

The original design of this investigation was to determine the retardation-effects of the various soluble chlorides. The

results, however, obtained for these salts, to be found further on, being of a rather anomalous character, the influence of sulphates was made the subject of a long series of experiments, the results obtained being contained in Table I.

Each experimental solution had a volume of 110 cubic centims., and contained ·3736 gram Fe″ as chloride, and 1·321 gram free HCl. To this was added 25 cubic centims. $KClO_3$ solution, equal to ·3406 gram, making the total volume $=135$ cubic centims., care being taken to have the solutions at the same temperature before mixing. From such a solution 10 cubic centims. were withdrawn, run into a small flask containing a few cubic centimetres of a nearly saturated solution of $MgSO_4$*, and titrated with permanganate.

The chemical conditions represented by these quantities of materials are

$$6\,FeCl_2 + (2\cdot5)KClO_3 + 6(5\cdot425)HCl.$$

The value for A was determined by diluting 10 cubic centims. of the stock solution of ferrous chloride $(=\cdot3736$ gram Fe″) to 135 cubic centims., and titrating 10 cubic centims. of this with the permanganate, the number of cubic centimetres required being taken as equal to 10·5, the value for A ; but although only approximately of this strength, the usual proportional corrections were made on the values for y for each experiment ; in which way all the experiments are rendered comparable with each other, as if performed with the same standard solution of permanganate.

Inserting these values of $\nu_1 = 2\cdot5$, $\nu_2 = 5\cdot425$, and $A = 10\cdot5$ in equation (3), it becomes

$$f\!\left(4\cdot425\,\log_{10}\frac{y+15\cdot75}{y} - 1\cdot5\,\log_{10}\frac{y+46\cdot46}{y}\right) = g + t. \quad (5)$$

The following three experiments will illustrate this formula, and how the retardation-effects are determined with magnesic sulphate as the retarding agent. Employing the first and third observations, the values obtained for f and g in equation (5) are 115·1 and 77·2 respectively ; and side by side with the observed values for t are the calculated quantities.

---

* Besides tending to stop the reaction, the addition of $MgSO_4$, the author has shown (Chemical News, vol. l.), renders the estimation of iron by permanganate in presence of free hydric chloride perfectly reliable. Mr. W. H. Deering has drawn attention to the fact that Zimmermann had previously proposed $MnSO_4$ for the same purpose.

Blank.   10° C.

Permanganate, y.	Time, minutes.	Time, calculated.
10·31	0	...
7·88	21·3	20·9
6·45	38·4	...
4·72	69·3	68·6
3·08	115·6	115·0
2·11	162·1	160·1
1·58	198·4	196·5
1·10	247·0	244·0

In a similar manner the values for f and g when 1 gram $MgSO_4$ was added, the total volume being the same as before, are found to be respectively 131·9 and 88·3.

1 gram $MgSO_4$.   Temp. 10° C.

Permanganate, y.	Time, minutes.	Time, calculated.
10·33	0	...
8·16	21·0	21·1
6·60	41·8	...
5·30	65·2	65·5
3·54	114·3	114·0
2·55	156·0	157·3
1·98	191·0	192·6
1·40	241·0	243·3

With 5 grams $MgSO_4$ the values found are $f = 201·3$ and $g = 134·6$.   5 grms $MgSO_4$.   Temp. 10° C.

Permanganate, y.	Time, minutes.	Time, calculated.
10·34	0	...
8·19	31·1	31·4
7·60	42·3	...
6·51	65·7	66·1
4·91	113·0	113·4
3·81	158·1	159·9
3·16	194·4	196·4
2·50	245·2	244·3

Now since f varies inversely as the rate of change, by comparing the above three values the ratios are found to be

$$115 \cdot 1 : 131 \cdot 9 : 201 \cdot 3 = 100 : 100 + 14 \cdot 6 : 100 + 5 \times 14 \cdot 9 ;$$

showing that the amount of oxidation that takes 100 minutes to be performed in the blank requires $114 \cdot 6$ minutes in the presence of 1 gram $MgSO_4$, and $174 \cdot 9$ minutes with 5 grams of the salt; or that the retardation is proportional to the quantity of the salt added, and equal to about $14 \cdot 7$ per cent. per gram. These three experiments are shown graphically in the figure.

Curves showing Retardation produced by 1 and 5 grams $MgSO_4$.
Temp. 10° C.
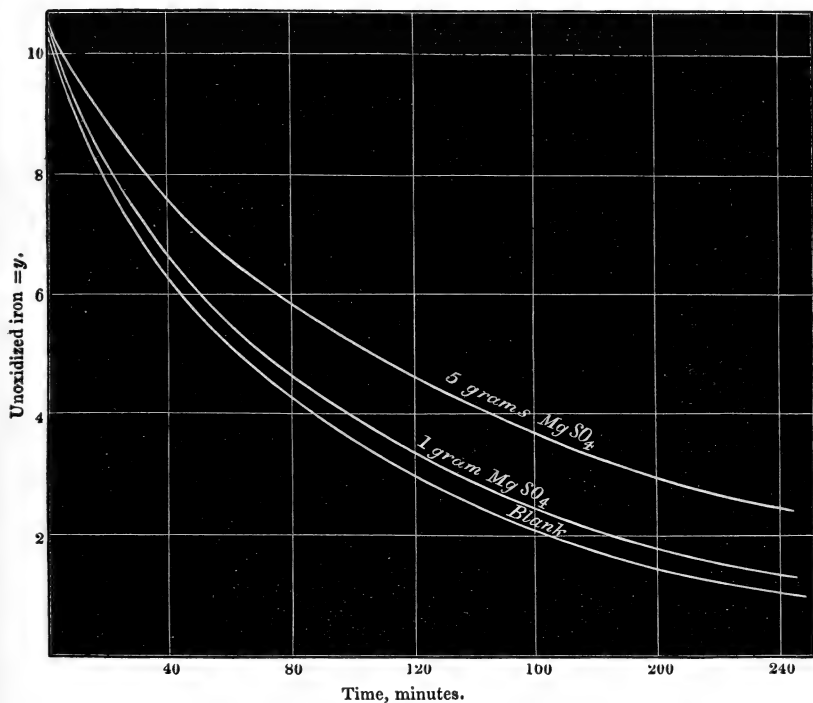
The following table contains the values of f and g for equation (5), the mean in each case of several experiments, when 2 grams of the various sulphates were employed, the temperature being in every case 10° C.

<div align="center">Table I.</div>

Salt, 2 grams.	*f.*	*g.*	Time to oxidize iron from y to y'.
Blank.........	115·8	77·2	100·0
Am_2SO_4.....	156·2	105·0	134·8
K_2SO_4	155·9	104·4	134·6
Na_2SO_4	155·4	104·2	134·2
Li_2SO_4	155·3	103·4	134·1
$MgSO_4$	148·7	99·2	128·4
$ZnSO_4$	141·3	94·1	122·0
$CdSO_4$	132·1	88·2	114·0

The noteworthy points exhibited by these numbers are that equal weights of the sulphates of ammonium, sodium, potassium, and lithium produce equal retardation-effects of approximately 17·2 per cent per gram ; whereas the sulphates of zinc, cadmium, and magnesium, metals usually grouped together in the same sense as the alkali ones, all produce different effects. If the percentage retardation produced by one gram of a salt be defined as its retardation-coefficient, the values for the above salts are, for the alkali group, 17·2 ; for $ZnSO_4$, 11 ; $CdSO_4$, 7 ; and for $MgSO_4$, 14·2.

The study of the influence of heat on the values of these retardation-coefficients it was considered would be of interest, in view of the general hypothesis regarding the intermolecular motions that take place in a chemical system, as well as the accelerating effect of heat upon these movements.

The numbers that are given in Table II. relate to $MgSO_4$, and are selected from a considerable number of experiments in which various sulphates were employed ; but the facts brought to light were all of the same general character as with $MgSO_4$.

In these experiments, instead of $2\frac{1}{2}$ molecules of chlorate only $1\frac{1}{2}$ was used, the equation representing the experiments being consequently

$$f\left(4·425 \log_{10} \frac{y+5·25}{y} - ·5 \log_{10} \frac{y+46·46}{y}\right) = g + t.$$

TABLE II.

Temp. C.	Blank.		2 grams MgSO$_4$.	
	f.	*g.*	*f'.*	*g'.*
6·13	366·7	152·7	478·6	199·3
10	256·4	106·4	335·8	139·7
13	193·7	80·7	256·6	106·9
17	134·3	56·3	178·7	74·7

The relations among these numbers are shown in the following table :—$\dfrac{f'}{f}$ gives the retardation produced by 2 grams MgSO$_4$ at the different temperatures, or the time required to oxidize the iron from y to y', being for the blank experiment equal to 100. In column a the values for α for the blank experiments are given, calculated on the assumption that the relation between rate of change and temperature is $\rho = \mu \alpha^\theta$, and in column b the values for α when the experiments are retarded by magnesic sulphate.

TABLE III.

Temp. C.	$\dfrac{f'}{f}.$	*a.*	*b.*
6·13	130·5		
10	130·9	1·097	1·096
13	132·4	1·098	1·094
17	133·0	1·096	1·095
Means	......	1·097	1·095

From the above table it is seen that the retardation-coefficient of MgSO$_4$ increases slightly with the temperature, from 15·2 at 6°·13 C. to 16·5 at 17° C., the rate of oxidation between these limits of temperature increasing about three-fold ; also that the rate increases in geometrical progression with temperature both in the blank and in the retardation experiments, the relation being in the former $\rho = \mu(1·097)^\theta$, and in the latter $\rho = \mu'(1·095)^\theta$. It has been shown* that

* Phil. Mag. October 1885.

when ferrous sulphate is oxidized by chlorate, the same relation $\rho = \mu(1 \cdot 093)^\theta$ holds good.

Chlorides.

When the present experiments were undertaken, the principal object in view was to determine the retardation-coefficients of the different chlorides; and it was conjectured that, with the evidence obtained from former experiments, these salts would be found to group themselves together as regards retardation-effects. Such a grouping, however, has not been found to exist. Indeed the anomalies that the experiments exhibit are of a very striking character. For instance, instead of a retardation, the presence of certain chlorides has been found to produce a considerable acceleration on the rate of oxidation ; whilst in another case, that of sodic chloride, neither retardation nor acceleration occurs.

Instead of employing quantities of iron, chlorate, and acid in accordance with equation (5), it was found that, by using only one molecule of chlorate and so rendering the rate much slower, the effects of the chlorides, being comparatively small, were better brought out. The acid being the same in amount as in the experiments with sulphates, or $v_2 = 5 \cdot 425$ and $A = 10 \cdot 5$, inserting these values in (4), the equation becomes

$$f\left(46 \cdot 46 - \frac{y}{\cdot 4343} \log_{10} \frac{y + 46 \cdot 46}{y}\right) = y(g + t).$$

In the following table are given the values for f and g, the means of several experiments, the temperature being 10° C.

Table IV.

Salt, 5 grams.	f.	g.	Time to oxidize iron from y to y'.
Blank.........	49·36	136·3	100
NaCl	49·72	136·9	100·8
KCl	60·30	166·3	122·2
AmCl.........	51·70	142·2	104·7
ZnCl$_2$.........	44·44	121·9	90·0
MgCl$_2$	40·65	111·9	82·3
CdCl$_2$	46·34	127·5	93·9

From these numbers it will be seen that no two chlorides give the same retardation-effects. Sodic chloride practically produces no effect whatever, whilst the chlorides of magnesium, cadmium, and zinc produce an *acceleration* of the rate

of oxidation. In the case of the sulphates, the retardation-effects of the three latter stand in order of magnitude thus : $MgSO_4 > ZnSO_4 > CdSO_4$; and the accelerations of the chlorides are seen to be in the same order—$MgCl_2 > ZnCl_2 > CdCl_2$.

In attempting to form a mental image of the state of matters in a chemical system undergoing change, it is customary to think of the moving parts or molecules, their velocities of translation, and the influence of various agencies, such as heat &c., increasing the velocities of the molecules and multiplying the chances of collision in a given time. Employing such language, it is easy to account for the retardation occasioned by the presence of chemically inactive substances in the system by saying that, by the motions of the molecules of such bodies, they interfere with the movements of the chemically active molecules by coming into collision with them ; in fact, continually getting in the way of the molecules of the several bodies undergoing chemical change, and so diminishing the number of impacts in a given time between the latter.

To such an explanation, however, the experiments in the first part of this paper are open to a grave objection. It might be argued, that the introduction of a sulphate into a solution of ferrous chloride in presence of much free HCl would give rise to such double decompositions as would account for the retardation observed in the rate of oxidation. If this were so, however, it is difficult to see how the retardation is the same in amount for equal weights of different sulphates, as well as proportional to the amount of the salt present, being the same result as was obtained with sulphates in a ferrous sulphate solution. In the experiments with chlorides no such double decompositions could occur, but here the results are anomalous. 5 grams of sodic chloride produce no effect whatever, whilst the same weight of the sulphate in ferrous chloride would give a retardation of 85 per cent., and in ferrous sulphate a retardation of 50 per cent. If retardation-effects are to be interpreted on the hypothesis of intermolecular movements and interference, and consequent diminution in the number of impacts, how comes it that so much sodic chloride produces no effect, whereas the same weight of potassic chloride causes a retardation of 22 per cent.? And, considering the subject in the same light, more remarkable still are the effects of magnesic, zincic, and cadmic chlorides, which produce an *acceleration* of the rate of oxidation, or increasing the number of collisions of the active bodies in a given time by an amount varying from 6 to 20 per cent. It seems difficult to account for such results on the hypothesis of interdiffusion and simple contact between the active molecules. Instances

of the difficulties that lie in the way of such a theory are exhibited by the great differences observed in the rates of somewhat analogous chemical changes. To take one example : how could such a theory explain the fact that, under suitable conditions of temperature and dilution, ferrous sulphate is oxidized by potassic chlorate at such a rate that only a fraction of the total work capable of being done is accomplished in ten thousand minutes, whereas permanganate performs the same work practically instantaneously ? Interdiffusion and simple contact among the active molecules alone would seem incapable of offering any explanation of this and similar facts ; at the same time it would be dangerous to speculate on the tendencies that chemical compounds undoubtedly possess to resist or undergo change under various conditions, in the face of the small amount of work that has been done bearing on chemical change.

In conclusion, I have to thank W. Crookes, Esq., F.R.S., for affording me facilities for performing the above experiments.

LIV. *Atmospheric Electricity.* *By* C. Michie Smith, *B.Sc.,* *F.R.S.E., F.R.A.S., Prof. Phys. Sc. Madras Christian College**.

IN 1882 I presented to the British Association a short report on observations made on atmospheric electricity in Madras, which, though few in number, were of some interest, as they seemed to show that negative electrification of the air was not necessarily associated with broken or stormy weather. At the same time it may be noted that the observations were by no means conclusive, as they were in each case followed by local showers which fell some hours afterwards. Since my return to India, however, I have obtained a large number of observations, many of which fully bear out the conclusion that, even in fine weather, the air may at times be highly charged with negative electricity.

Neglecting a few single observations, the first series obtained was in September 1883, when, on twelve days between the 3rd and 25th, negative readings were recorded. At the time that these readings were taken I thought they were in some way connected with the green sun and the wonderful sunglows which appeared that month ; and an account of them will be found in my paper on these phenomena in the Transactions of the Royal Society of Edinburgh, vol. xxxii. p. 389. More recent observations have, however, shown that, under

certain meteorological conditions, similar readings may always be expected.

The following table gives the electrometer-readings at 10 A.M., along with the observations of wind-direction, moisture, and rainfall made at the same hour at the Madras observatory.

TABLE I.
Observations at 10 hours M.M.T.   September 1883.

Date.	Electro- meter- readings.	Percentage of satura- tion.	Wind- direction.	Rain in past 24 hours.	Remarks.
				inch.	
1.	....	56	W.	0·01	
2.	....	57	W.S.W.	0·01	
3.	....	47	W.		
4.	− 241	55	W.		
5.	− 93	44	W.		
6.	− 310	55	W.S.W.		
7.	+ 16	64	S.W.	0·03	Cloudy and cool.
8.	− 6	46	W.S.W.	......	Rain at 7 P.M.
9.	+ 16	53	W.S.W.	0·03	Morning cool and cloudy.
10.	− 21	61	W.S.W.		
11.	− 13	55	W.N.W.	......	Cloudy, but hot.
12.	− 70	49	W.	......	Thin haze ; much dust.
13.	+ 18	53	W.	......	{ Distant lightning in early morn- ing. Local showers in the afternoon.
14.	− 11	56	W.S.W.		
15.	?	49	W.N.W.		
16.	?	55	W.N.W.		
17.	?	73	S.S.W.		
18.	+	69	W.S.W.		
19.	?	50	W.		
20.	− 34	44	N.W.		
21.	− 19	49	W.		
22.	− 4	51	W.		
23.	?	52	W.N.W.		
24.	− 25	62	W.N.W.	......	Bright.
25.	− 15	57	W.N.W.	... ..	Cloudy.
26.	+ 6	63	N.N.W.	......	Dull and hazy.
27.	+ 5	59	S.E.		
28.	+	56	S.W.	0·04	
29.	?	58	W.S.W.		
30.	?	72	W.N.W.	0·45	

Note.—Column 2 gives the difference between the earth-readings and air-readings in divisions of the scale, of which about 24 = 110 volts.

Neglecting cases occurring in broken weather, the next negative readings were got in March 1884. During that month negative readings were obtained on six days, and on each occasion the weather was bright and the wind south-westerly; and no rain fell in Madras on these days, nor, in

fact, until nearly a fortnight after the last negative reading
was observed. The readings in April and the first half of
May were all normal; and during the next two months
absence from Madras prevented me from continuing the
observations, which were not renewed till July 14. Between
the 14th and 31st of July the readings were negative on
seven days. On only one of these days did any rain fall at
the place of observation, and then only 0·04 inch fell some
eight hours after. In each case the wind was westerly, and
in most cases raised great clouds of dust.

During August negative readings were obtained on nine
days, and on none of these could the negative potential be
traced to storms at or near the place of observation. On
August 1, for instance, the readings were negative from
11 A.M. to 2 P.M., and no rain fell till 4 P.M. on the 2nd; on
the 28th they were negative from noon to 5 P.M., ranging
from 8 to 467 divisions (say 37 to 2140 volts), and no rain
fell till the morning of the 31st. The following table (II.)
shows the observations at 10 A.M.

TABLE II.
Observations at 10 hours M.M.T.　　August 1884.

Date.	Electro-meter-readings.	Percentage of satura-tion.	Wind-direction.	Rain in past 24 hours.	Remarks.
				inch.	
1.	+27	85	S.S.W.	0·11	
2.	−34	44	W.		
3.	−95	45	W.N.W.		
4.	−71	47	W.N.W.		
5.	−12	56	W.N.W.	0·07 {	Thunderstorm and rain at night south of Madras.
6.	?	62	W.	0·62	
7.	+ 2	56	W.N.W.		
8.	− 3	56	W.		
9.	−26	50	N.N.W.		
10.	−17	48	N.W.		
11.	+32	55	N.		
12.	+27	51	N.N.W.		
13.	+24	78	S.W.	0·59	
14.	+ 7	69	W.N.W.	......	Reading −4 at 7 A.M.
15.	+10	84	W.S.W.	1·01	
16.	+66	79	W.S.W.	1·85	
17.	+30	68	W.S.W.	0·40	
18.	?	77	W.S.W.	0·16	
19.	+ 6	61	W.N.W.	0·09	
20.	?	62	W.	0·11	
21.	− 4	60	W.		
22.	0	68	W.S.W.	0·09 {	Reading negative at 11 A.M. and noon.
23.	−35	66	W.		
24.	− 9	58	W.		

It will be noticed that the effect of a shower is to make the succeeding readings positive; and generally it is found that negative readings are got only when the ground is dry and also warm; for on a bright morning the readings become negative earlier than when the morning is cloudy.

In September there were negative readings on 13 days almost entirely during bright fine weather.

TABLE III.

Observations at 10 hours M.M.T.   September 1884.

Date.	Electro-meter-readings.	Percentage of satura-tion.	Wind-direction.	Rain in past 24 hours.	Remarks.
				inch.	
1.	+27	85	S.S.W.	......	0·16 in. rain fell on August 31st.
2.	−16	44	W.		
3.	−95	45	W.N.W.		
4.	−72	47	W.N.W.	......	Shower at 4 P.M.
5.	−12	56	W.N.W.	0·07	Evening thunder-storm, with heavy rain at sea 12 miles off Madras.
6.	?	62	W.	0·62	
7.	+ 2	56	W.N.W.	......	Negative reading at 11 A.M.
8.	− 3	56	W.		
9.	− 8	50	N.N.W.		
10.	−17	48	N.W.		
11.	+32	55	N.		
12.	+27	51	N.N.W.		
13.	+24	78	S.W.	0·59	
14.	+ 7	69	W.N.W.		
15.	+47	84	W.S.W.	1·01	Rain and thunder in early morning. Thunder-storm at night.
16.	+40	79	W.S.W.	1·85	
17.	+23	68	W.S.W.	0·40	
18.	?	77	W.S.W.	0·16	
19.	+29	61	W.N.W.	0·09	
20.	?	62	W.	0·11	
21.	− 4	60	W.		
22.	0	68	W.S.W.	......	Negative reading at 11 A.M.
23.	−33	66	W.		
24.	− 9	58	W.		

From September 24, 1884, to May 14, 1885, only one negative reading has been obtained in fine weather.

Looking over the tables of electrometer-readings, the first feature that strikes one is that in only one case is the potential negative before 9 A.M.; and that in most cases, if the potential is positive at 10 A.M., it remains positive all day, though on one or two occasions when a low positive reading was obtained at 10 A.M., a negative one was obtained at 11 or 12

o'clock. Again, in all cases mentioned above, the negative readings were got with a westerly wind, which in Madras is usually very dry, having blown over a large extent of flat dry land. Whenever the wind veered round so as to blow in the least degree from the sea, the potential at once became positive. This has been well marked in all cases, and when the sea-breeze came on early in the day no negative readings were obtained ; but when, as happened on several occasions, the sea-breeze was delayed till late in the afternoon, even then negative readings continued till the wind veered round. An important question is, What is the influence of the clouds of dust that are usually flying on days when we get negative readings ? This is a question which I have not yet been able to answer fully; but certain observations tend to show that there is an intimate connection between the presence of dust and the negative electrification of the air. Many observations were made extending over 10 to 20 minutes: and it was almost invariably found that the negative electrification was strongest during gusts of dust-laden air. At such times the potential would often run up so rapidly that it was impossible to measure it accurately, while during lulls it would often fall almost to zero. The mere friction of the dry dust against the match and insulated umbrella would not account for this ; for the potential began to increase rapidly before the dust-cloud actually reached the place of observation. Again, it was found that higher negative readings were got when the observations were made on the ground than when they were made on the roof of a house ; and, further, that in parts of the town where there was little dust, negative readings were rare, and were never very high. Too much stress must not be laid on this last point, for simultaneous observations could not be carried out at two places, as I had only one electrometer. A number of observations have been made in dust with south-easterly and north-easterly winds ; but the air was never found to be negatively electrified. This may be explained readily enough as due simply to the presence of moisture ; for one of the earliest facts impressed on an experimenter on static electricity in this part of India is that, however well an electric machine may work, or a Leyden jar hold its charge, while a westerly wind is blowing, the moment the wind veers round to the east the Leyden jar loses its charge almost at once and the electric machine ceases to act, be it a Holtz, a Voss, or a Wimshurst, or any other machine warranted to work " in all weathers."

When the weather becomes sufficiently dry I intend to make some direct experiments on the action of dust, and on the height to which the negative electrification extends.

I have found it impossible, unaided, to carry out a suffi-
ciently complete series of observations to get the diurnal curve
during these times of land wind; but the accompanying dia-
gram may be taken as a first approximation to it between the
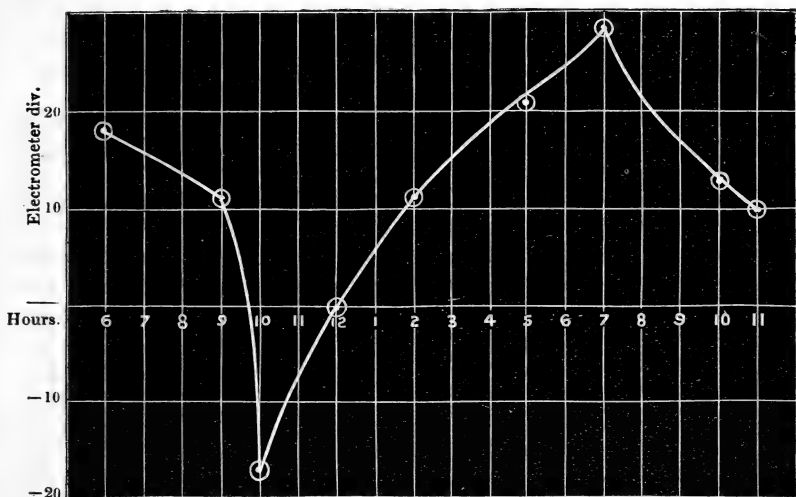
hours of 6 A.M. and 11 P.M.   It is prepared from the observa-
tions of September 1883 and August and September 1884.

Madras, July 16, 1885.

LV. *Notices respecting New Books.*

*Handbook of Technical Gas-analysis, containing concise Instructions
for carrying out Gas-analytical Methods of Proved Utility.   By
CLEMENS WINCKLER, Ph.D., Professor of Chemistry at the Frei-
burg Mining Academy.   Translated, with a few additions, by
GEORGE LUNGE, Ph.D., Professor of Technical Chemistry at the
Federal Polytechnic School, Zurich.   Van Voorst.   London.*

TO those who have, during the last eight or ten years, been under
the necessity of analyzing the gaseous mixtures from the flues
of regenerative furnaces, and there are many such persons in this
country, the name of Dr. Winckler is favourably known as being
one of the first so to simplify the operations as to render it un-
necessary to employ the methods of Bunsen and Regnault.   The
translator is, we think, scarcely aware of the extent to which tech-
nical gas-analysis is cultivated in England; for, in his preface, he
says that " it is now quite usual, at any rate in Germany, to perform
technical gas-analysis, not merely in chemical works, but for testing
the efficiency of steam-boiler furnaces and such purposes.   In
England some of these processes have also been introduced; but
they are not as yet known and appreciated to the same extent
as abroad."   It would of course be difficult, if not impossible, to
compare the actual number of analyses made in the two countries;
but we have no hesitation in saying that Dr. Bunte's process, at all

events, is well known, thoroughly appreciated, and frequently employed for analyzing the gases from regenerative furnaces in this country.

In this little work of 125 pages the author has succeeded in condensing so large an amount of information that any chemist, even if previously entirely unaccustomed to the analysis of gaseous mixtures, may, with a moderate amount of practice, soon find himself in a position to undertake the analysis of flue gases.

One of the great advantages of the new method is that water is made to supersede mercury in the various manipulations; the extent to which this substitution does away with the necessity for personal skill in the operator can only be appreciated by those who have had to analyze gases by the older processes.

The author very properly commences by describing the apparatus employed by him in sampling the gases to be examined, and the directions given are so complete as to leave nothing to be desired; on the other hand, a properly educated chemist would never have any difficulty in devising a method of withdrawing a portion of gas from a flue or chamber, and storing it in a convenient vessel from which small quantities could be removed as required. It must be remembered, however, that the work is intended by the author for the instruction of students and others who have not previously acquired skill in gas-analysis. Among the devices described is Bonny's automatic aspirator, which he has patented in Germany. This instrument appears to us to have advantages which will make it extremely useful under many circumstances. The chapter on the measurement of gases will be found very useful, especially to those who are unacquainted with the methods commonly employed in scientific researches. The author (p. 30) states that " Gasmeters are never altogether reliable; but they give serviceable approximate figures, especially if merely the number of revolutions is noticed as shown by the dials, without looking for the absolute volume of the gas passed." To this we may add that, although the best gas-meters in this country are very well made, and quite sufficient for every technical purpose unconnected with refined analysis, it is very difficult to adjust even the most expensive ones to a less error than one third of a per cent. on the total volume of the gas passed.

We think the author might with advantage have omitted the description of his own gas-burette, as it is admitted to have been superseded by newer and better forms.

The descriptions of Honigmann's, Bunte's, and Orsat's apparatus are given clearly; and the same remark applies to the ingenious gaspipettes of Hempel, founded, we believe, on that of Doyère.

Altogether this is a very valuable little work, and is absolutely indispensable to every chemist who undertakes the technical analysis of gases. The author is to be congratulated on the excellence of the typography and the admirable manner in which the engravings have been reproduced. For the fidelity of the translation the name of Dr. Lunge is a sufficient guarantee.

LVI. *Intelligence and Miscellaneous Articles.*

ON THE SEPARATION OF LIQUID ATMOSPHERIC AIR INTO TWO DIFFERENT LIQUIDS. BY S. WROBLEWSKI.

IN my note of April 13, 1885, I had occasion to remark that the laws of the liquefaction of atmospheric air are not those of the liquefaction of a simple gas, and that air behaves like a mixture the components of which are subject to different laws of liquefaction. If at first sight liquid air seems to behave in such fashion that we might speak of the critical point of air, that arises simply from the slight difference there is between the curves of the tension of the vapour of oxygen and of nitrogen. Thus we may designate the pressures between 37 and 41·3 atmospheres and the temperatures between $-140°·8$ and $-143°$ as defining the critical point of air. The curve of the tensions of air depends, among other circumstances, on the manner in which the quantity of the liquid is used for the experiment. Much more does this curve cease to have any significance when we obtain temperatures of $-190°$ C., and especially at still lower temperatures. Thus with air liquefied under high pressures, and then liberated and exposed to the pressure of only one atmosphere, the boiling-point rises gradually from $-191°·4$ to $-187°$ C., and that owing to a change in the composition of the liquid. As nitrogen evaporates more rapidly than oxygen, the temperature of the boiling liquid tends towards $-181°·5$ C., which is the boiling-point of pure oxygen.

Still more striking are the special features shown by air evaporated in oxygen, as seen from the following Table :—

Temperature.	Pressure in centim.	Temperature.	Pressure in centim.	Temperature.	Pressure in centim.
$-195°·02$	...	$-196°·65$	...	$-198°·6$	3·8
196·2	...	196·65	12·4	198·2	...
197·1	...	196·65	11	197·9	3·6
197·5	...	196·55	10	197·85	...
197·6	...	196·1	...	197·85	3·5
197·6	...	196·0	...	198·05	...
197·6	...	196·95	...	198·5	3·2
197·5	16·1	198	4·4	198·75	...
197·5	...	198·6	...	199·28	...
197·38	15·2	198·65	4·1	199·55	3·0
197·15	...	198·8	4	199·8	...
196·85	14·6	198·99	...	200	2·8

While the tension of the vapours of liquids evaporated by the pump diminishes steadily, the temperature, as shown in the Table for equidistant intervals of time, passes through a series of maxima and minima; under low pressures it ultimately attains values which are scarcely higher than those of pure oxygen at the same pressure. In these conditions the air only contains a very small quantity of nitrogen.

But this is not all. Air can give two distinct liquids, different in appearance and in composition, forming two separate layers

separated by a perfectly visible meniscus. I have attained this result by the following method :—Having liquefied at − 142° C. a certain quantity of air in the tube of the apparatus which I employ for using permanent gases as cooling mixtures, I allow a quantity of gaseous air to enter the tube, such that the pressure of the gas having become equal to 40 centim. and its optical density equal to that of the liquid, the meniscus entirely disappears, after which I slowly lessen the pressure ; the moment the manometer indicates a pressure of about 37·6 atmospheres, I see that a new meniscus forms at a point in the tube much higher than the place previously occupied by the vanished meniscus. A few minutes afterwards the first meniscus reappears at the place at which we had seen it disappear, and at the same moment two liquids are distinctly seen, different in character, one on the top of the other. The two liquids remain separated for several seconds. After this a current of very small bubbles forms, which ascend, detaching themselves from the meniscus which separates the two liquids. In consequence of this phenomenon the upper liquid becomes a little opaque ; the meniscus, gradually destroyed by the current, ultimately disappears altogether, and the last result is a single liquid homogeneous in appearance. *

By means of a small metal tube introduced into the apparatus I have been able, without destroying the meniscus, to take at will either from the bottom or top layer a quantity of liquid sufficient for analysis. While the lower liquid contains 21·28 to 21·5 of oxygen, the upper one only contained 17·3 to 18·7.

This experiment is of great importance in the theory of the critical state of gases. It shows in fact, contrary to the assertion made some years ago by certain physicists, that the disappearance of the meniscus of a liquid, when it is obtained by increasing the pressure exerted by a gas on a superposed liquid, does not effect a solution of the liquid in the gas.—*Comptes Rendus,* Sept. 28, 1885.

ON THE SOURCE OF THE HYDROGEN OCCLUDED BY ZINC DUST.
BY GREVILLE WILLIAMS, F.R.S.

In my paper "On the Synthesis of Trimethylamine and Pyrrol from Coal-Gas, and on the Occlusion of Hydrogen by Zinc Dust,"† I showed that, under certain conditions, zinc dust behaved towards hydrogen like palladium ; and I inferred, from the phenomena observed, that the zinc dust occluded hydrogen at ordinary temperatures, and gave it off in an active condition when heated. In my second paper, "Note on the Occlusion of Hydrogen by Zinc Dust and the Meteoric Iron of Lenarto " ‡, I gave the results of determi-

---

* In this experiment air, which is a completely colourless liquid, shows moreover a singularly enigmatical optical phenomenon, which immediately precedes the appearance of the upper meniscus. The part of this tube where the meniscus should form, assumes a feebly orange coloration, which disappears the moment the meniscus appears. A like phenomenon never precedes the appearance of the lower meniscus, which separates the two liquids.

† See 'Journal of Gas Lighting,' vol. xlv. p. 15.   ‡ *Loc. cit.* p. 485.

nations of the amount occluded in the dust by direct heating, and also by combustion with cupric oxide. I likewise made the suggestion that the hydrogen, in the cases both of the dust and the meteorite, had probably been originally derived from water, and not necessarily, in the latter case, from the meteorite having at one time been exposed to an atmosphere of hydrogen at a high pressure. The present paper is to be regarded as a study of the effect of water, in the forms of liquid and vapour, upon the amount of hydrogen occluded. As my later determinations were made on a fresh specimen of the commercial dust, I considered it necessary, in the first place, to determine the volume of the hydrogen contained in it. In the course of the experiments it was found, on leaving the apparatus to repose after the hydrogen had been expelled, that the volume of the mixture of gas and air in the measuring-tube gradually diminished; and this is one cause of the variations in the amounts obtained in the earlier experiments. Variations in the volumes are also caused by differences in the temperatures to which the retorts containing the zinc dust are exposed; and, at an early stage of the experiments detailed in this paper, I was led to finally abandon the use of soft glass in favour of retorts made from combustion-tubing.

Determination of the Hydrogen contained in a Fresh Sample of the Zinc Dust.

Experiment I.—6·4790 grammes of a fresh sample of zinc dust were heated in a soft glass retort to as high a temperature as it would bear. The arrangements were precisely the same as in the experiments detailed in my second paper. The reason why I continued to use 6·4790 grammes (100 grains) was because this amount had been previously found to occupy the volume of one cubic centim. All volumes are reduced to a temperature of 60° Fahr. (15°·55 C.) and a pressure of 30 inches of mercury; and a correction is made for the volume of that portion of the exit tube of the retort which enters the measuring-apparatus. The graduated tube before the experiment contained 46·8 cubic centim. of air. After the apparatus had cooled to the atmospheric temperature, the volume was found to be 78 cubic centim. This gives 31·2 cubic centim. for the hydrogen expelled from 1 cubic centim. of the zinc dust at the temperature at which the experiment was made. This is the lowest result yet obtained, and was doubtless due to insufficient heating.

Experiment II.—In this experiment 6·4790 grammes were heated in a horizontal retort made from hard combustion-tubing. The air in the measuring-tube before heating amounted to 7·3 cubic centim. After heating and subsequent cooling to atmospheric temperature the volume was 44·1 cubic centim.; after deducting the air we have 36·8 cubic centim. from 1 cubic centim. of zinc dust. This result approximates pretty closely to the experiment in my second paper, which gave 37·5 cubic centim.

Experiment III.—In this experiment the utmost heat of the lamp was continued for a long time—until, in fact, there was no indica-

tion of any trace of gas being expelled ; and the volume was read off directly the retort had cooled to the temperature of the laboratory, thus preventing reabsorption. The hydrogen after all corrections amounted to 46·4 cubic centim.

Experiment IV.—In a fourth experiment, made like the last, 47·4 cubic centim. were obtained.

We now have the following values for the volumes of hydrogen expelled from the new sample of commercial zinc dust :—

					cubic centim.
I. Soft glass retort, measured next day				......	31·2
II. Hard glass retort, measured when cooled				..	36·8
III. „	„	„	„	..	46·4
IV. „	„	„	„	..	47·4

The volume in the last experiment is the largest I have been able to obtain, and shows that ordinary commercial zinc dust may contain nearly fifty times its volume of hydrogen.

Effect of Wetting on the Amount of Hydrogen Occluded.

Experiment I.—I took the usual amount of zinc dust (6·4790 grammes) and thoroughly wetted it with boiling water. On drying it in the water-oven until the weight was constant it was found to have increased by 0·1924 gramme. The retort was then charged with 6·4790 grammes of the dried dust, and heated in a retort made from combustion-tubing. The air in the measuring-tube before the experiment amounted to 3·9 cubic centim. The volume of hydrogen evolved, after deducting the air and making all corrections, amounted to 89·4 cubic centim., or 42 cubic centim. more than in the highest result obtained from unwetted zinc dust. This very large increase in the yield of hydrogen as compared with any of the experiments made with the original zinc dust points very clearly to the source whence it was obtained, and strongly tends to confirm the view thrown out in my second paper, that this source was water. It was again found in this experiment that it required the highest heat of the lamp to drive off the last traces of hydrogen, and it was observed that during the operation a certain amount of water was produced. On keeping the apparatus in the state in which it was left after the experiment, it was found that the volume of the gas and air in the measuring-tube became less day by day, until, at the expiration of a fortnight, it only measured 80·4 cubic centim. The absorption therefore amounted to 9 cubic centim. As the air in the measuring-tube only amounted to 3·9 cubic centim., it became evident that the absorption was chiefly, if not entirely, due to hydrogen. So that we have now conclusive proof that zinc dust, in addition to taking up water and giving up its hydrogen on heating, absorbs this gas at ordinary temperatures when surrounded by it in a moist condition, thus confirming the conclusion arrived at in my first paper from the phenomena observed during the synthesis of trimethylamine. Whether it absorbs the gas when it is in an anhydrous state I propose to determine later on.

Experiment II.—In a second experiment 6·4790 grammes of the

dust, on being saturated with boiling water and then dried in the water-oven until the weight was constant, gave an increase of 0·1561, or 0·0363 gramme less than in the first experiment. I then subjected 6·4790 grammes to a dull red heat ; and the resulting gas, in two hours after the operation, measured when all corrections were made, gave 89 cubic centim., or 8·4 cubic centim. more than in the last experiment. The two highest experiments with unwetted zinc dust gave 46·4 cubic centim. and 47·4 cubic centim., the mean being 46·9. The two with wetted zinc dust gave 89·4 and 89 cubic centim. The mean of these is 89·2, or only 4·6 cubic centim. less than double the amount from unwetted zinc dust.

It is proper to notice that the increase of weight of the zinc dust on wetting and subsequent drying in the first experiment was 0·1924 gramme, and in the second 0·1561 gramme. The mean of these is 0·1742. Now, if 10 atoms of zinc ($65·3 \times 10$) had fixed 1 molecule of water, the increase would be 0·1785—a number so near to the mean of the experiments as probably not to be entirely without meaning ; but, on the other hand, I have not yet had time to analyze the zinc dust, which, of course, cannot be taken as representing even moderately pure zinc.

Effect of Exposure of Zinc Dust to a Moist Atmosphere.

Having shown that the wetted dust after drying gives off nearly double as much hydrogen as was evolved from it in the condition in which it was received, it became important to know how the hydrogen had been occluded by the dust which had not been wetted. It has long been known that shippers are unwilling to carry large quantities of zinc dust in their vessels, owing to the danger of its getting wetted, in which case it becomes heated to an extent which may become dangerous. It being, therefore, extremely improbable that the specimens with which I worked had ever been wetted, or even rendered damp purposely, it struck me that it had probably absorbed moisture from the atmosphere. This would perfectly account for the presence of hydrogen in the commercial product ; and, owing to its being kept closely packed, for the amount being small as compared with that contained in the dust which had been thoroughly wetted. To determine the question I placed 6·4790 grammes in a watch-glass over a vessel containing water, the whole being then covered by a bell-glass. The apparatus was kept in a room having a nearly constant temperature of about 72° Fahr. It was weighed almost every day from the commencement of the experiment (Aug. 6) until the 17th of September, by which time it had ceased to increase. It was found that for the first fourteen days it gained about 3 centigrammes a day ; the next fourteen days the increase fell to about $1\frac{1}{2}$ centigrammes a day ; and after this it gradually diminished, and at last entirely ceased. It was then dried in the water-oven until the weight became constant. The substance which had caked together was then pulverized and taken for the following experiments.

Experiment I.—One quarter of the usual amount, namely 1·6198 grammes, was heated in a similar manner to the previous experi-

ments.   The corrected volume of hydrogen was 85·3 cubic centim., which multiplied by 4 gives no less than 341·2 cubic centim. of hydrogen from 6·4790 grammes.   This is about seven times the amount afforded by the original dust, and 3·8 times more than the mean of the results obtained with the dust which had been wetted.

Experiment II.—In this experiment, in which the full heat of a strong Bunsen flame was kept until the volume of hydrogen ceased perceptibly to increase, 90·7 cubic centim. of hydrogen were obtained from 1·6198 grammes, or 362·8 cubic centim. from 6·4790 grammes=100 grains.

The above results confirm in the strongest manner the views I had entertained as to the source of the hydrogen in zinc dust, and conclusively show that exposure to a moist atmosphere at a moderate temperature is eminently favourable to the condensation of the hydrogen.   It is not improbable that, by suitably modifying the conditions, this amount may be exceeded.   As zinc dust thus charged with hydrogen can hardly fail to become an important chemical reagent, I shall endeavour to determine the maximum amount that can be occluded, and the ratio to the amount of metallic zinc present.—*Journal of Gas Lighting*, Oct. 13, 1885.

ON TWO NEW TYPES OF CONDENSING HYGROMETERS.
BY M. G. SIRE.

The accuracy of condensing hygrometers is known to depend on the exactitude with which we observe the temperature of the surface on which dew is deposited as well as on the more or less distinct perception of this deposit.

I have succeeded in rendering these determinations very distinct by observing the deposit of aqueous vapour on a cylindrical or a plane brilliant surface, which gives rise to two new types of condensing hygrometer, where the fall of temperature is produced by the evaporation of ether in which is a thermometer.

The reservoir of the first type consists of a cylindrical tube of thin polished metal, the ends of which are insulated in the *interior* by two pieces of ebonite, so that the volatile liquid is only in contact with the metal side by a middle zone of about 1 centim. in height.   On this zone the dew is deposited; it shows itself by a whitish ring which appears at half the height of the reservoir.

The reservoir of the second is entirely of ebonite; it is traversed laterally by a circular aperture closed by a thin metal disk, polished on the inside.   On the part of this disk which closes the aperture the dew is deposited, forming a dull white circle in the centre; under a certain angle the disk appears of a pure black.

The bright surfaces are obtained by an electrochemical deposit of palladium; the black polish of this metal reveals the slightest traces of condensation.

The essential character of these hygrometers is that the deposit is made in the centre of a brilliant metal surface without a break. On the other hand, the agitation of the liquid and the thinness of the sides ensures perfect equality of the two parts in each instrument.— *Comptes Rendus*, Sept. 28, 1885.

LVII. *On the Dilatancy of Media composed of Rigid Particles in Contact. With Experimental Illustrations.* By Professor Osborne Reynolds, *LL.D., F.R.S.*[*]

[Plate X.]

IDEAL rigid particles have been used in almost all attempts to build fundamental dynamical hypotheses of matter: these particles have generally been supposed smooth.

Actual media composed of approximately rigid particles exist in the shape of sand, shingle, grain, and piles of shot; all which media are influenced by friction between the particles.

The dynamical properties of media composed of ideal smooth particles *in a high state of agitation* have formed the subject of very long and successful investigations, resulting in the dynamical theory of fluids. Also the limiting conditions of equilibrium of such media as sand have been made the subject of theoretical treatment by the aid of certain assumptions.

These investigations, however, by no means constitute a complete theory of granular masses; nor does it appear that any attempts have been made to investigate the dynamical properties of a medium consisting of smooth hard particles, held in contact by forces transmitted through the medium. It has sometimes been assumed that such a medium would possess the properties of a liquid, although in the molecular hypothesis of liquids now accepted the particles are assumed to be in a high state of motion, holding each other apart by

---

[*] Communicated by the Author. This Paper was read before Section A of the British Association at the Aberdeen Meeting, September 10, 1885, and again before Section B, at the request of the Section, September 15.

collisions; such motion being rendered necessary to account for the property of diffusion.

Without attempting anything like a complete dynamical theory, which will require a large development of mathematics, I would point out the existence of a singular fundamental property of such granular media which is not possessed by known fluids or solids. On perceiving something which resembles nothing within the limits of one's knowledge, a name is a matter of great difficulty. I have called this unique property of granular masses "dilatancy," because the property consists in a definite change of bulk, consequent on a definite change of shape or distortional strain, any disturbance whatever causing a change of volume and generally dilation.

In the case of fluids, volume and shape are perfectly independent; and although in practice it is often difficult to alter the shape of an elastic body without altering its volume, yet the properties of dilation and distortion are essentially distinct, and are so considered in the theory of elasticity. In fact there are very few solid bodies which are to any extent dilatable at all.

With granular media, the grains being sensibly hard, the case is, according to the results I have obtained, entirely different. So long as the grains are held in mutual equilibrium by stresses transmitted through the mass, every change of relative position of the grains is attended by a consequent change of volume; and if in any way the volume be fixed, then all change of shape is prevented.

In speaking of a granular medium, it is assumed to be in such a condition that the position of any internal particle becomes fixed when the positions of the surrounding particles are fixed.

This condition is very generally fulfilled, but not always where there is friction; without friction it would be always fulfilled.

From this assumption it at once follows that no grain in the interior can change its position in the mass by passing between the contiguous grains without disturbing these; hence, whatever alterations the medium may undergo, the same particle will always be in the same neighbourhood.

If, then, the medium is subject to an internal strain, the shapes of the internal groups of molecules will all be altered, the shape of each elementary group being determined by the shape of the surrounding particles. This will be rendered most intelligible by considering instances; that of equal spheres is the most general, and presents least difficulty.

A group of such spheres being arranged in such a manner

that, if the external spheres are fixed, the internal ones cannot move, any distortion of the boundaries will cause an alteration of the mean density, depending on the distortion and the arrangement of the spheres. For example :—

If arranged as a pile of shot (Plate X. fig. 2), which is an arrangement of tetrahedra and octahedra, the density of the media is $\dfrac{1}{\sqrt{2}}\dfrac{\pi}{3}$, taking the density of the sphere as unity.

If arranged in a cubical formation, as in fig. 1, the density is $\dfrac{\pi}{6}$, or $\sqrt{2}$ times less than in the former case.

These arrangements are both controlled by the bounding spheres ; and in either case the distortion necessitates a change of volume.

Either of these forms can be changed into the other by changing the shape of the bounding surface.

In both these cases the structure of the group is crystalline, but that is on account of the plane boundaries.

Practically, when the boundaries are not plane, or when the grains are of various sizes or shapes, such media consist of more or less crystalline groups having their axes in different directions, so that their mean condition is amorphous.

The dilation consequent on any distortion for a crystalline group may be definitely expressed. When the mean condition is amorphous, it becomes difficult to ascertain definitely what the relations between distortion and dilation are. But if, when at maximum density, the mean condition is not only amorphous but isotropic, a natural assumption seems to be that any small contraction from the condition of maximum density in one direction means an equal extension in two others at right angles.

As such a contraction in one direction continues, the condition of the medium ceases to be isotropic, and the relation changes until dilation ceases. Then a minimum density is reached ; after this, further contraction in the same direction causes a contraction of volume, which continues until a maximum density is reached. Such a relation between the contraction in one direction and the consequent dilation would be expressed by

$$ e - 1 = e_1 \sqrt{\sin^2 \frac{a}{e_1}} \; ; $$

e being the coefficient of dilation, a that of contraction, and e_1 the maximum dilation ; the $+$ve root only to be taken.

The amorphous condition of minimum volume is a very stable condition ; but there would be a direct relation between

the strains and stresses in any other condition if the particles were frictionless and rigid.

If the particles were rigid the medium would be absolutely without resilience, and hence the only energy of which it would be susceptible would be kinetic energy ; so that, supposing the motion slow, the work done upon any group in distorting it would be zero. Thus, supposing a contraction in one direction and expansion at right angles, then if p_x be the stress in the direction of contraction, and p_y, p_z the stress at right angles, a being the contraction, b and c expansions,

$$p_x a + p_y b + p_z c = 0 \; ;$$

or, supposing $b = c$, $p_y = p_z$,

$$p_x a + p_y (a + c) = 0.$$

With friction the relation will be different ; the friction always opposes strain, *i. e.* tends to give stability.

It is a very difficult question to say exactly what part friction plays ; for although we may perhaps still assume without error,

$$\frac{p_y}{p_x} = \frac{1 - \sin \phi}{1 + \sin \phi},$$

where ϕ is the angle of repose, we cannot assume that $\tan \phi$ has any relation to the actual friction between the molecules.

The extreme value of ϕ is a matter of arrangement ; as in the case of shot, which would pile equally well although without friction.

Supposing the grains rigid, the relations between distortion and dilation are independent of friction ; that is to say, the same distortion of any bounding surfaces must mean the same internal distortion whatever the friction may be.

The only possible effect of friction would be to render the grains stable under circumstances under which they would not otherwise be stable ; and hence we might with friction be able to bring about an alteration of the boundaries other than the alteration possible without friction ; and thus we might possibly obtain a dilation due to friction. How far this is the case can be best ascertained by experiment.

In the case of a granular medium, friction may always be relaxed by relieving the mass of stress, and any stability due to this cause would be shown by shaking the mass when in a condition of no stress.

But before applying this test, it is necessary to make perfectly sure that during the shaking the boundary spheres do not change position.

Another test of the effect of friction is by comparing the

relative dilation and distortion with different degrees of friction. If the dilation were in any sense a consequence of friction, it would be greater when the coefficient of friction between the spheres was greater. Where the granular mass is bounded by solid surfaces, the friction of the grains against these surfaces will considerably modify the results.

The problem presented by frictionless balls is much simpler than that presented in the case of friction. In the former case the theoretical problem may be attacked with some hope of success. With friction the property is most easily studied by experiment.

As a matter of fact, if we take means to measure the volume of a mass of solid grains more or less approximately spheres, the property of dilatancy is evident enough, and its effects are very striking, affording an explanation of many well-known phenomena.

If we have in a canvas bag any hard grains or balls, so long as the bag is not nearly full it will change its shape as it is moved about; but when the sack is approximately full a small change of shape causes it to become perfectly hard. There is perhaps nothing surprising in this, even apart from familiarity; because an inextensible sack has a rigid shape when extended to the full, any deformation diminishing its capacity, so that contents which did not fill the sack at its greatest extension fill it when deformed. On careful consideration, however, many curious questions present themselves.

If, instead of a canvas bag, we have an extremely flexible bag of india-rubber, this envelope, when filled with heavy spheres (No. 6 shot), imposes no sensible restraint on their distortion; standing on the table it takes nearly the form of a heap of shot. This is apparently accounted for by the fact that the capacity of the bag does not diminish as it is deformed. In this condition it really shows us less of the qualities of its granular contents than the canvas bag. But as it is impervious to fluid, it will enable me to measure exactly the volume of its contents.

Filling up the interstices between the shot with water so that the bag is quite full of water and shot, no bubble of air in it, and carefully closing the mouth, I now find that the bag has become absolutely rigid in whatever form it happened to be when closed.

It is clear that the envelope now imposes no distortional constraint on the shot within it, nor does the water. What, then, converts the heap of loose shot into an absolutely rigid body? Clearly the limit which is imposed on the volume by the pressure of the atmosphere.

So long as the arrangement of the shot is such that there is enough water to fill the interstices the shot are free, but any arrangement which requires more room is absolutely prevented by the pressure of the atmosphere.

If there is an excess of water in the bag when the shot are in their maximum density, the bag will change its shape quite freely for a limited extent, but then becomes instantly rigid, supporting 56 lb. without further change. By connecting the bag with a graduated vessel of water so that the quantity which flows in and out can be measured, the bag again becomes susceptible of any amount of distortion.

Getting the bag into a spherical form and its contents at maximum density, and then squeezing it between two planes, the moment the squeezing begins the water begins to flow in, and flows in at a diminishing rate until it ceases to draw more water.

The material in the bag is in a condition of minimum density under the circumstances. This does not mean that all the parts are in a condition of minimum density because the distortion is not the same in all the parts ; but some parts have passed through the condition of maximum while others have not reached it, so that on further distortion the dilations of the latter balance the contractions of the former. If we continue to squeeze, water begins to flow out until about half as much has run out as came in ; then again it begins to flow in. We cannot by squeezing get it back into a condition of uniform maximum density, because the strain is not homogeneous. This is just what would occur if the shot were frictionless ; so that it is not surprising to find that, using oil instead of water, or, better (on account of the india-rubber), a strong solution of soap and water, which greatly diminishes the friction, the results are not altered.

On measuring the quantities of water, we find that the greatest quantity drawn in is about 10 per cent. of the volume of the bag ; this is about one third of the difference between the volumes of the shot at minimum and maximum density.

$$\frac{1}{\sqrt{2}} : 1, \text{ or 30 per cent. of the latter.}$$

On easing the bag it might be supposed that the shot would return to their initial condition. But that does not follow : the elasticity of form of the bag is so slight compared with its elasticity of volume, that restitution will only take place as long as it is accompanied with contraction of volume.

So long as the point of maximum volume has not been

reached, approximate restitution follows quite as nearly as could be expected, considering that friction opposes restitution. But when the squeezing has been carried past the point of maximum volume, then restitution requires expansion; and this the elasticity of shape is not equal to accomplish, so that the bag retains its flattened condition. This experiment has been varied in a great variety of ways.

The very finest quartz sand, or glass balls $\frac{3}{4}$ inch in diameter, all give the same results. Sand is, on the whole, the most convenient material, and its extreme fineness reduces any effect of the squeezing of the india-rubber between the interstices of the balls at the boundaries; which effect is very apparent with the balloon bags, and shot as large as No. 6.

A well-marked phenomenon receives its explanation at once from the existence of dilatancy in sand. When the falling tide leaves the sand firm, as the foot falls on it the sand whitens, or appears momentarily to dry round the foot. When this happens the sand is full of water, the surface of which is kept up to that of the sand by capillary attraction; the pressure of the foot causing dilation of the sand, more water is required, which has to be obtained either by depressing the level of the surface against the capillary attraction, or by drawing water through the interstices of the surrounding sand. This latter requires time to accomplish, so that for the moment the capillary forces are overcome; the surface of the water is lowered below that of the sand, leaving the latter white or dryer until a sufficient supply has been obtained from below, when the surface rises and wets the sand again. On raising the foot it is generally seen that the sand under the foot and around becomes momentarily wet; this is because, on the distorting forces being removed, the sand again contracts, and the excess of water finds momentary relief at the surface.

Leaving out of account the effect of friction between the balls and the envelope, the results obtained with actual balls, as regards the relation between distortion and dilation, appear to be the same as would follow if the balls were smooth.

The friction at the boundaries is not important as long as the strain over the boundaries is homogeneous, and particularly if the balls indent themselves into the boundaries, as they do in the case of india-rubber. But with a plane surface the balls at the boundaries are in another condition from the balls within. The layer of balls at the surface can only vary its density from $2/\sqrt{3}$ to 1. This means that the layer of balls at a surface can slide between that surface and the adjacent layer, causing much less dilation than would be caused

by the sliding of an internal layer within the mass. Hence where two parts of the mass are connected by such a surface, certain conditions of strain of the boundaries may be accommodated by a continuous stream of balls adjacent to the surface. This fact made itself evident in two very different experiments.

In order to examine the formation which the shot went through, an ordinary glass funnel was filled with shot and oil, and held vertical while more shot were forced up the spout of the funnel. It was expected that the shot in the funnel would rise as a body, expanding laterally so as to keep the funnel full. This seems to have been the effect at the commencement of the experiment ; but after a small quantity had passed up it appeared, looking at the side of the funnel, that the shot were rising much too fast, for which, on looking into the top of the funnel, the reason became apparent. A sheet of shot adjacent to the funnel were rising steadily all round, leaving the interior shot at the same level with only a slight disturbance.

In another experiment one india-rubber bag was filled with sand and water ; at the centre of this ball was another much smaller ball, communicating through the sides of the outer envelope by means of a glass pipe with an hydraulic pump. It was expected that, on expanding the interior ball by water, the sand in the outer ball would dilate, expanding the outer ball and drawing more water into the intervening sand. This it did, but not to the extent expected. It was then observed that the outer envelope, instead of expanding, generally bulged in the immediate neighbourhood of the point where the glass tube passed through it ; showing that this tube acted as a conductor for the sand from the immediate neighbourhood of the interior ball to the outer envelope, just as the glass sides of the funnel had acted for the shot.

As regards any results which may be expected to follow from the recognition of this property of dilatancy,—

In a practical point of view, it will place the theory of earth-pressures on a true foundation. But inasmuch as the present theory is founded on the angle of repose, which is certainly not altered by the recognition of dilatancy, its effect will be mainly to show the real reason for the angle of repose.

The greatest results are likely to follow in philosophy, and it was with a view to these results that the investigation was undertaken.

The recognition of this property of dilatancy places a hitherto unrecognized mechanical contrivance at the command of those who would explain the fundamental arrangement of the universe, and one which, so far as I have been

able to look into it, seems to promise great things, besides possessing the inherent advantage of extreme simplicity.

Hitherto no medium has ever been suggested which would cause a statical force of attraction between two bodies at a distance. Such attraction would be caused by granular media in virtue of this dilatancy and stress. More than this, when two bodies in a granular medium under stress are near together, the effect of dilatancy is to cause forces between the bodies in very striking accordance with those necessary to explain coherence of matter.

Suppose an outer envelope of sufficiently large extent, at first not absolutely rigid, filled with granular media, at its maximum density. Suppose one of the grains of the media commences to grow into a larger sphere; as it grows, the surrounding medium will be pushed outwards radially from the centre of the expanding sphere. Considering spherical envelopes following the grains of the medium, these will expand as the grains move outwards. This fixes the distortion of the medium, which must be contraction along the radii, and expansion along all tangents.

The consequent amount of dilation depends on the relation of distortion and dilation, and on the arrangement of the grains in the medium. At first the entire medium will undergo dilation, which will diminish as the distance from the centre increases. As the expansion goes on, the medium immediately adjacent to the sphere will first arrive at a condition of minimum density; and for further expansion this will be returning to a maximum density, while that a little further away will have reached a minimum. The effect of continued growth will therefore be to institute concentric undulations of density from maximum to minimum density, which will move outwards; so that after considerable growth the sphere will be surrounded with a series of envelopes of alternately maximum and minimum density, the medium at a great distance being at maximum density. At a definite distance from the centre of the sphere not more than

$$1.4R,$$

where R is the radius of the sphere, the density will be a minimum, and between this and the sphere there may be a number of alternations depending on the relative diameters of the grains and the spheres.

The distance between these alternations will diminish rapidly as the sphere is approached. The distance of the next maximum is $1.2R$, the next minimum is given by $1.09R$, and the next maximum $1.06R$.

The general condition of the medium around a sphere which has expanded in the medium is shown in Plate X. fig. 3, which has been arrived at on the supposition that the sphere is large compared with the grains.

From a radius about 1.4 R outwards the density gradually increases, reaching a maximum density at infinity; and at all distances greater than 1.8 R the law is expressed by

$$\frac{de}{dr} = \frac{1}{r^n},$$

where n has some value greater than 3 depending on the structure of the medium.

Within the distance 1.4 R the variation is periodic, with a rapidly diminishing period. In this condition, supposing the medium of unlimited extent and the sphere smooth, the sphere may move without causing further expansion, merely changing the position of the distortion in the medium; for the grains, slipping over the sphere, would come back to their original positions. It thus appears that smooth bodies would move without resistance if the relation between the size of the grains and bodies is such that the energy due to the relative motion of the grains in immediate proximity may be neglected. The kinetic energy of the motion of the medium would be proportional to the volume of the ball multiplied by the density of the medium and the square of the velocity.

But the momentum might be infinite supposing the medium infinite in extent, in which case a single sphere would be held rigidly fixed.

If we suppose two balls to expand instead of one, and suppose the distortion of the medium for one ball to be the same as if the other were not there, the result will be a compound distortion. Since, however, the dilation does not bear a linear relation to the distortion, the dilation resulting from the compound distortion will not be the sum of the dilations for the separate distortions unless we neglect the squares and products of the distortions as small.

Supposing the bodies so far apart that one or other of the separate distortions caused at any point is small, then, retaining squares and products, it appears that the resultant dilation at any point will be less than the sum of the separate dilations by quantities which are proportional to the products of the separate distortions.

The integrals of these terms through the space bounded by spheres of radii R and L are expressed by finite terms, and terms inversely proportional to L, which latter vanish if L is

infinite. Thus, while the total separate dilations are infinite, the compound dilations differ from the sum of the separate by finite terms, and these are functions of the product of the volumes and the reciprocal of the distance.

Assuming stress in the medium, the difference in the value of these finite terms for two relative positions of the bodies multiplied by the stresses, represents an amount of work which must be done by the bodies on the medium in moving from one position to another.

To get rid of the difficulty of infinite extent of medium, if for the moment we assume the envelope sufficiently large and imposing a normal pressure upon the medium, then, since the work done will be proportional to the dilation, the force between the bodies will be proportional to the rate at which this dilation varies with the distance between them.

The force between the bodies would depend on the character of the elasticity as well as on the dilation.

It is not necessary to assume the outer envelope elastic; this may be absolutely rigid and one or both the balls elastic.

In such case the two balls are connected by a definite kinematic relation. As they approach they must expand, doing work which is spent in producing energy of motion ; as they recede, the kinetic energy is spent in the work of compressing the balls.

As already stated, the momentum of the infinite medium for a single ball in finite motion may be infinite, and proportional to the product of the volume of the ball by the velocity ; but with two balls moving in opposite directions, with velocities inversely as the masses, the momentum of the system is zero. Therefore such motion may be the only motion possible in a medium of infinite extent.

When the distance between the balls is of the same order as their dimensions, the law of attraction changes with the law of the compound dilations and becomes periodic, corresponding to the undulations of density surrounding the balls. Thus, before actual contact were reached, the balls would suffer alternate repulsion and attraction, with positions of equilibrium more or less stable between, as shown in figs. 4 and 5 (Pl. X.).

We have thus a possible explanation of the cohesion and chemical combination of molecules, which I think is far more in accordance with actual experience than anything hitherto suggested.

It was the observation of these envelopes of maximum and minimum density which led me to look more fully into the property of dilatancy.

The assumed elasticity of the surrounding envelope, or of the balls, has only been introduced to make the argument clear.

The medium itself may be supposed to possess kinetic elasticity arising from internal distortional motion, such as would arise from the transmission of waves in which the motion of the medium is in the plane of their fronts.

The fitness of a dilatant medium to transmit such waves is only less striking than its property of causing attraction, because in the first respect it is not unique.

But as far as I can see such transmission is not possible in a medium composed of uniform grains. If, however, we have comparatively large grains uniformly interspersed, then such transmission becomes possible. If, notwithstanding the large grains, the medium is at maximum density, the large grains will not be free to move without causing further dilation; and it seems that the medium would transmit distortional vibrations in which the distortions of the two sets of grains are opposite.

Such waves, although the motion would be essentially in the plane of the wave, would cause dilation, just as waves in a chain cause contraction in the reach of the chain. They would in fact impart elasticity to the medium, exactly as, in the case of a slack chain having its ends fixed but otherwise not subject to forces, any lateral motion imparted to the chain will cause tension proportional to the energy of disturbance divided by the slackness or free length of chain.

Distortional waves therefore, travelling through dilatant material which does not quite occupy the space in which it is confined when at maximum density, would render the medium uniformly elastic to distortion, but not in the same degree to compression or extension. The tension caused by such waves would depend on the gross energy of motion of the waves divided by the total dilation from maximum density consequent on the wave-motion. All such waves, whatever might be their length, would therefore move with the same velocity.

If, when rendered elastic by such waves, the medium were thrown into a state of distortion by some external cause, this would diminish the possible dilation caused by the waves. Thus work would have to be done on the medium in producing the external distortion which would be spent in increasing the energy of the waves. For instance, the separation of two bodies in such a medium, which, as already shown, would increase the statical distortion, would increase the energy of the waves and *vice versâ*.

As far as the integrations have been carried for this condition of elasticity, it appears, with a certain arrangement of

large and small grains, that the forces between the bodies would be proportional to the product of the volumes divided by the square of the distance ; *i. e.* that the state of stress of the medium may be the same as Maxwell has shown must exist in the æther to account for gravity. We have thus an instance of a medium transmitting waves similar to heat-waves and causing force between bodies similar to the forces of gravitation and cohesion, in such a manner as to constitute a conservative system. More than this, by the separation of the two sets of grains, there would result phenomena similar to those resulting from the separation of the two electricities. The observed conducting power of a continuous surface for the grains of a medium closely resembles the conduction of electricity. And such a composite medium would be susceptible of a state in which the arrangement of the two sets of grains were thrown into opposite distortions, which state, so far as it has yet been examined, appears to coincide with the state of a medium necessary to explain electrodynamic and magnetic phenomena according to Maxwell's theory.

In this short sketch of the results which it appears to me may follow from the recognition of the property of dilatancy, I have not attempted to follow the exact reasoning even so far as I have carried it.

In the preliminary acceptance of a theory the mind must be guided rather by a general view of its adaptability than by its definite accordance with some out of many observed facts. And as it seems, after a preliminary investigation, that in space filled with discrete particles, endowed with rigidity, smoothness, and inertia, the property of dilatancy would cause amongst other bodies not only one property but all the fundamental properties of matter, I have, in pointing out the existence of dilatancy, ventured to call attention to this dilatant or kinematic theory of æther without waiting for the completion of the definite integrations, which must take long, although it is by these that the fitness of the hypotheses must be eventually tested.

LVIII. *On the Refraction of Fluorine.* By GEORGE GLADSTONE, *F.C.S.*[*]

IN his paper on the Refraction-Equivalents of the Elements, published in the Phil. Trans. of 1869, Dr. Gladstone estimated the equivalent of fluorine at 1·45, from the results

of an observation taken of a solution of fluoride of potassium. He gave it, however, with all reserve, remarking at the same time that " fluor-spar and kryolite gave very small values for fluorine, or rather indicate that this body has scarcely any influence on the rays of light." In the same paper he gives the specific refractive energy as $0 \cdot 073$, which corresponds to the refraction-equivalent given above. As it stands, it is by far the lowest on the list, none of the other elements having a specific refraction of less than $0 \cdot 1$; but had it been calculated from the results given by the minerals above mentioned, the specific refraction would have been as low as $0 \cdot 016$.

As the discrepancy then noted was so very wide, and special interest attaches to fluorine in this connection on account of its singularly small refractive power, I have thought it worth while to review all the evidence upon the subject, and to obtain new observations of a solution of fluoride of potassium.

Brewster gives $1 \cdot 344$ and $1 \cdot 349$ as the index of refraction of kryolite. The mean of these will give $24 \cdot 63$ as the refraction-equivalent for $Na_3Al_2F_6$. Deducting $13 \cdot 2$ for the sodium and $9 \cdot 7$ for the aluminium, which is the most recent value assigned to this metal, there will only be $1 \cdot 73$ left for six atoms of fluorine. Thus fluorine equals $0 \cdot 29$.

Of fluor-spar there are several independent observers. Brewster gives $1 \cdot 436$ for the index of refraction for the bright part of the spectrum; and Wollaston $1 \cdot 433$. Fizeau gives $1 \cdot 435$ for the line D; Stephan, in 1871, gives $1 \cdot 4339$; and Kohlrausch, in 1878, gives $1 \cdot 4324$ and $1 \cdot 4342$ for the same. The average of these is $1 \cdot 4341$, which, taking the specific gravity at $3 \cdot 183$, according to Landolt's tables, will give a refraction-equivalent of $10 \cdot 64$ for CaF_2. Deducting $10 \cdot 0$ for the calcium, fluorine will equal $0 \cdot 32$.

I am indebted to my brother for a redetermination of the aqueous solution of fluoride of potassium, which gives $8 \cdot 15$ as the refraction-equivalent for the line A; deducting $7 \cdot 85$ for the potassium, the fluorine equals $0 \cdot 30$.

These are all closely accordant.

Messrs. Topsoe and Christiansen have taken the indices of refraction and the specific gravities of a series of crystalline fluorides of uniform composition. They are biaxial crystals; and the observations are given by them for the lines C, D, and F of the spectrum, both of the ordinary and extraordinary ray. In the following table I have taken the mean of the two rays for F, and give also the mean value for A calculated from the differences between the indices for the lines C and F. The refraction-equivalent of the substance is given for

the line A, and the last column contains the value for fluorine obtained by deducting the amount due to the other elements, viz. 35·556 for the water, 7·4 for the silicon, 11·5 for copper, 9·9 for nickel, 9·8 for zinc, 6·7 for magnesium, and 11·5 for manganese, and then dividing the residue by six. The refraction-equivalents for the above-named elements are taken from the revised list published in the 'American Journal of Science' for January 1885.

Substance.	Specific gravity.	Index, F.	Index, A.	Refraction-equivalent, A.	Refraction-equivalent of Fluorine.
$CuF_2, SiF_4, 6H_2O$ ...	2·182	1·4131	1·4049	58·16	0·62
$NiF_2, SiF_4, 6H_2O$ ...	2·109	1·4027	1·3935	57·60	0·79
$ZnF_2, SiF_4, 6H_2O$ ...	2·104	1·3926	1·3857	57·80	0·84
$MgF_2, SiF_4, 6H_2O$...	1·761	1·3553	1·3493	54·35	0·78
$MnF_2, SiF_4, 6H_2O$...	1·858	1·3690	1·3621	59·44	0·83

Four out of the five will be seen to give closely accordant results, and agree well with the general average, which is 0·77.

The same observers give similar data for a silico-ammonio-fluoride, $2NH_4F, SiF_4$, which is a uniaxial crystal. The index for the line F is 1·3723, and the calculated figure for the line A is 1·3670. The specific gravity being 1·970, the refraction-equivalent will be 33·16. The latest estimate for NH_4 being 11·1, there will be 3·56 left to satisfy the six atoms of fluorine, after deducting what may be due to the other elements. This gives 0·59 for fluorine; which is, as near as possible, the mean of all the observations here examined.

This still leaves a range of from 0·3 to 0·8 ; but in any case the refraction-equivalent is of exceedingly small amount; and the specific refraction, even at the highest limit, can scarcely be the half of that of any other substance known. Thus, while the specific refraction of chlorine, bromine, and iodine amounts to 0·279, 0·191, and 0·193 respectively, that of fluorine will lie between 0·015 and 0·044, as calculated from the extreme results of the observations recorded above.

LIX. *On Measurements of the Intensity of the Horizontal Component of the Earth's Magnetic Field made in the Physical Laboratory of the University of Glasgow.* By THOMAS GRAY, *B.Sc., F.R.S.E.**

[Plate XI.]

IN the course of some measurements of the horizontal component of the intensity of the earth's magnetic field, which have recently been made in the physical laboratory of the University of Glasgow, several improvements in the apparatus and mode of conducting these experiments suggested themselves. The following paper is a description of these measurements.

The method adopted was, in general principle, that of Gauss; that is, the determination by a deflection-experiment of the ratio M / H, and by an oscillation-experiment of the product MH, where M is the magnetic moment of a magnet, called in this description the *deflector*, and H is the horizontal intensity of the earth's magnetic field at the place of experiment. The earlier experiments, of which the results are given below, were, with the exception of the mode of determining the effective length of the deflector, conducted in the way that has for several years been practised in Sir William Thomson's laboratory, and descriptions of which have already been published†.

THE DEFLECTION EXPERIMENT consists in finding the deflection produced by the deflector on a second needle, called the *magnetometer-needle*, suspended at a known distance from it, and thus furnishing an equation of the form

$$\frac{M}{f(2a_1, r)} = H \tan \theta ; \quad \ldots \ldots \quad (1)$$

where $f(2a_1, r)$ is a function of $2a_1$ the effective length of the deflector, and r the distance between the centre of the deflector and the centre of the magnetometer-needle, and θ is the angle of deflection. The function $f(2a_1, r)$ depends on the relative direction of the line joining the centres of the deflector and magnetometer-needles, the direction of the axis of the deflector and the direction of the lines of force in the magnetic field, and on the distribution of magnetism in the deflector and magnetometer-needles. Strictly $f(2a_1, r)$ should be $f(2a_1, b, r)$,

where b is the length of the magnetometer-needle ; but it is one of the merits of the method here described that the magnetometer-needle is made so short that its magnetic length may be neglected, and the resulting equation thus much simplified.

The positions adopted in these determinations were, for the line joining the centres of the deflector and the magnetometer-needle, the magnetic meridian and a line at right angles to it ; and for the direction of the magnetic axis of the deflector, a line at right angles to the magnetic meridian. We then have for the former of these positions,

$$f(2a_1, r) = \frac{(r^2 - a_1^2)^2}{2r} ; \quad \cdots \quad (2)$$

and for the latter position,

$$f(2a_1, r) = (r_1^2 + a_1^2)^{\frac{3}{2}}. \quad \cdots \quad (3)$$

From equation (1) we obtain, by (2) and (3),

$$\frac{M}{H} = \frac{(r^2 - a_1^2)^2}{2r} \tan \theta_0, \quad \cdots \quad (4)$$

and

$$\frac{M}{H} = (r_1^2 + a_1^2)^{\frac{3}{2}} \tan \theta_1. \quad \cdots \quad (5)$$

Now, besides M and H, the value of a_1 is also unknown ; but when θ_0 and θ_1 are determined at nearly the same time, we can calculate a_1 from the above equations. We have clearly

$$\frac{(r^2 - a_1^2)^2}{2r(r_1^2 + a_1^2)^{\frac{3}{2}}} = \frac{\tan \theta_1}{\tan \theta_0}. \quad \cdots \quad (6)$$

Expanding the numerator and denominator on the left-hand side of the above equation, and neglecting small terms, we readily obtain, as a close approximation,

$$a_1^2 = \frac{\theta_0 r^3 - 2\theta_1 r_1^3}{2\theta_0 r + 3\theta_1 r_1}. \quad \cdots \quad (7)$$

There is in the method here described a departure from the usual practice—namely, determining the effect of the length of the deflector and deflected magnets, by double and triple experiments with the deflector placed at different distances along a line through the centre of the deflected magnet. In the first place, the third experiment is rendered unneces-

sary by making the deflected magnet so short that its magnetic length may be neglected ; and, in the second place, the effect of the length of the deflector is found by adopting two positions for which the length enters in the resulting equations (4) and (5) above, with opposite sign, rendering the observation highly sensitive to that effect. By adopting this method a good estimate of the effective length of different deflectors is obtained ; and this is useful information outside of the particular object of the experiment.

The latest form and arrangement of the apparatus for the deflection-experiment is shown in Pl. XI. fig. 1, where T is the table on which the apparatus is placed, M the magnetometer, A and B the deflector-stands, and C the scale on which the deflections are read. The magnetometer M consists of a light mirror about ·8 centim. in diameter, on the back of which two magnets, 1 centim. long and ·08 centim. in diameter, are fixed. A better form of needle would, as has been pointed out by Sir William Thomson, be two thin disks of hard steel mounted with their planes parallel and at a distance apart somewhat less than the diameter of the disk.

The mirror with attached magnets is suspended by a single silk fibre (half a cocoon-fibre) in a recess cut in a block of wood, W. Two holes at right angles to each other, and passing through the position of the mirror and magnets, allow the magnetic system to be accurately adjusted when setting up the apparatus. The holes, with the exception of that in front of the mirror, are plugged while the instrument is in use, and the mirror and fibre are protected from currents of air by means of a plate of plane glass. The sole plate, P, is furnished with three brass feet, which rest on a " hole, slot, and plane " arrangement cut in the top of the glass plate, *p*, fixed to the table. The deflector-stands, A and B, consist of a base plate of mahogany furnished, as in the case of the magnetometer, with three brass feet which rest on " hole, slot, and plane " arrangements cut in the glass plate *p*. A centre pivot, *c*, is fixed in the sole plate and passes through a closely-fitting hole in the glass plate, *g*, which rests on three thin blocks of hard wood and is free to turn in azimuth. A strip of wood having a V-groove cut along its upper side and furnished with an adjusting-screw, *s*, is cemented to the top of the glass plate *g* in such a way that the bottom of the V-groove is vertically above the centre of the pivot *c*. The screw, *s*, gives an adjustment for the centre of the magnet, which is necessary if the magnets differ slightly in length. The centre of the magnet is seldom exactly at the middle of the length of the bar, but, with the arrangement here adopted, the adjustment

can be readily made by turning the screw *s* until equal deflections are obtained on opposite sides of zero, when the deflector is reversed by turning the plate *g* through 180° in azimuth. The deflectors, *d*, are shown in positions east and west of the magnetometers; and the distance between their centres when in this position is 70 centim. Two plates similar to *p* are placed, one on the north and one on the south side of the magnetometer, in such a position that, when the deflector-stand is resting on them, the distance between the centres of the deflectors is 60 centim., and the line joining them is in the magnetic meridian. The feet on which the deflector-stands rest are so adjusted that the deflectors are equidistant from the magnetometers, and at the same distance apart when the positions of the stands are interchanged. The scale C is graduated to millimetres on glass, and is placed with its centre directly in front, and in the focus, of the magnetometer-mirror. The distance between the scale and the mirror is 129 centim.

A paraffin-lamp, with a copper funnel which has a vertical slit in front, with a fine wire in its centre, covered by a plane glass plate, is placed behind the scale, and furnishes a beam of light which is focused on the glass scale by the magnetometer-mirror. The scale being transparent, the deflections can be read either from the back or the front of it. When the deflections were read from behind the scale, it was found convenient, although not absolutely necessary, to render the glass partially obscure; and this, acting on a suggestion of Mr. Bottomley, was done by dusting lycopodium-powder over it. The deflections were taken in the following manner :—

The table T was first placed in such a position that the line joining the centres of A and B (Pl. XI. fig. 1) was exactly at right angles to the magnetic meridian. This was done in one or other of the following ways :—(1) A thin wire was passed under the magnetometer and stretched along the line joining the centres of A and B, and then taken back, either over the top of the magnetometer, or beneath and at a greater distance from it, in such a way as to form a vertical plane circuit. An electric current was then sent through the circuit, and the table turned until it produced no deflection on the magnetometer-needle. (2) One of the deflectors was placed in its position north or south of the magnetometer, and lifted out of its V by the suspension-fibre. The table was then turned until the suspended needle produced no deflection of the magnetometer-needle. When this is the case, the direction of the magnetic axes of the deflector and the magnetometer-needle are in the same line; and if the latter needle be in its proper position, this line also passes through the centre of the deflector when placed on the

other side of the magnetometer.   To ensure that this was the case, the deflector was placed on the other side and the position of the table for no deflection again observed.   The magneto-meter-needle was then adjusted, by turning the levelling-screws, until the two positions were coincident.   A combination of the methods (1) and (2) gives a ready means of testing whether the plates g have been properly placed on the table.

Suppose A to be east and B west of the magnetometer. The deflectors were turned by means of the plate g until their lengths were accurately in the magnetic east and west line, and their poles so placed as to produce a deflection to the same side of zero.   The deflection was then read.   The plates g were next turned through $180°$ and the deflection on the opposite side of zero read.   The plates g were then turned back to their first position, and the deflection again read.   The difference between the mean of the first and third reading and the second gives twice the deflection.   The same operation was then repeated with A north and B south, with A west and B east, and with A south and B west.   The mean of the deflections for the east and west positions and the mean of the deflections for the north and south positions were then found, and from them the mean effective length of the two deflectors calculated.   This length was then substituted in equations (11) and (12) below, and the value of H calculated.

Previous to the adoption of the above apparatus only one deflector was used, and it was placed by hand in the positions necessary for a cycle of operations similar to that above described.   The idea of using two deflectors placed on opposite sides of the magnetometer, and the arrangement for them shown in fig. 1, is due to Sir William Thomson.   It has the advantage of greater symmetry, it allows the deflector to be placed at a greater distance from the magnetometer, and, what is most important, the magnet need not be handled during the experiment.

THE OSCILLATION EXPERIMENT consists in finding the period of oscillation of the deflector when suspended with its axis horizontal, and free to perform horizontal oscillations under the influence of the earth's magnetic field.   This experiment gives the value of MH from the equation

$$MH + x = \frac{4\pi^2\mu}{P^2}. \quad \cdots \cdots \quad (8)$$

The quantity x refers to the torsional rigidity of the suspension, which was practically zero in these experiments; μ is the moment of inertia of the oscillating system, and P the

period of oscillation. The following is a description of the
arrangement and the mode of observation.

A length of single cocoon-fibre was taken, and a stirrup
like that shown at S (fig. 2) formed on one end of it by fold-
ing it twice, so as to make four fibres, and making a knot
about 3 centim. from the end. The other end was passed
through a small hole in the brass bow, b (fig. 1), and then
fixed to a small strip of sheet lead which simply rested on the
sole plate and held the deflector in the proper position. The
deflector was placed in the stirrup S, and the loops adjusted
so as to suspend it horizontally. The magnet was thus sus-
pended in a stirrup almost devoid of inertia, and by a fibre of
negligible torsional rigidity. This leaves μ, the moment of
inertia of the deflector, and P, its period of oscillation, to be
determined. The moment of inertia can be very accurately
calculated from the mass, length, and thickness of the bar,
when, as is the case with these deflectors, the bar is a round
cylinder of small and perfectly uniform diameter. Greater
accuracy in these calculations, and the advantage of small
diameter in the "side on" position when taking deflections, are
the main reasons, apart from simplicity, why a solid cylinder
is preferred to a thin tube for the deflector. The period of
oscillation P was in the earlier experiments obtained either by
observing, with the eye placed behind a narrow slit, the times
of successive transits of the end of the bar across a fixed mark
(usually a black thread stretched vertically near the end of
the magnet and in the same magnetic meridian) ; or by ob-
serving the times of the successive transits across the vertical
wire of a telescope. In the later experiments, one end of the
deflector was polished with the view of using it as a mirror to
reflect a beam of light to a scale placed at some distance.
This method was not successful, owing to defects in the mirror,
and it has been abandoned in favour of a light silvered-glass
mirror, m (fig. 1), about 0·3 centim. in diameter and 0·01
gramme in weight, attached to the stirrup with its plane
parallel to the length of the magnet. The same lamp and scale
are thus available both for oscillation and deflection experi-
ments. With this arrangement the amplitude of the oscilla-
tion need never exceed one degree, and hence no correction
for arc is necessary.

With regard to the effect of the inertia of the mirror on μ,
it is to be remarked that its total moment of inertia is about
·001, while that of the deflector is about 40 ; so that, even if
the inertia of the mirror be neglected, the error is not more
than $\frac{1}{400}$ per cent.

When a second observer was available, time was usually

taken from a watch with a centre seconds hand moving over
a dial divided to quarter-seconds. The watch was keeping
almost perfect time. In this case an observer counted the
oscillations of the magnet, and called *now* at the end of every
four or five periods, while the other observer noted the time.
Personal error does not enter into this method, as it is elimi-
nated in taking the differences. When the transits and time
were taken by the same observer, the time was taken from a
chronometer beating half-seconds. The observer took time,
say, at the beginning of a minute, and then counted the beats
until he could observe a transit. By simply counting the
number of beats between two successive transits, the total
number of periods in one minute could then be estimated; and
the time of the first transit after each minute was then taken
as long as the amplitude was sufficiently large to allow the
time to be accurately estimated. Fractions of half seconds
were estimated from the position of the magnet at the beat
next before and next after transit.

The results of the different observations of time were com-
bined in the following manner :—First suppose an even
number $2n$ observations to have been taken. The sum of the
intervals of time between the nth and the $(n+1)$th, the $(n-1)$th
and the $(n+2)$th, and so on to the 1st and $2n$th, divided by
the square of the number of intervals, and by the number of
periods between each pair of observations, gives the average
period as nearly as it can be obtained from that set of obser-
vations. Suppose next an odd number $2n+1$ observations to
have been taken. The sum of the intervals between the 1st
and the $(n+1)$th, the 2nd and $(n+2)$th, and so on to the nth
and $(2n+1)$th, each divided by the corresponding number of
periods, divided by the number of intervals, gives the average
period. Two sets of observations were usually taken; and if
they agreed closely, the mean of the two was assumed to be
the true period.

We have then the following equations for the determination
of H when one deflector only is used :—

$$\frac{M}{H} = \frac{(r^2 - a_1^2)^2}{2r} \tan \theta_0, \quad \ldots \ldots \quad (4)$$

$$\frac{M}{H} = (r_1^2 + a_1^2)^{\frac{3}{2}} \tan \theta_1, \quad \ldots \ldots \quad (5)$$

and

$$MH = \frac{4\pi^2 \mu}{P^2}$$

$$= \frac{8}{3} \frac{\pi^2 \left(a^2 + \frac{3}{64} d^2\right) w}{P^2}, \quad \ldots \ldots \quad (8)$$

where $2a$ is the length, d the diameter, and w the weight of the deflector-bar. From (4) and (8) we obtain,

$$H^2 = \frac{8}{3}\, \frac{\pi^2\left(a^2 + \frac{3}{64}\,d^2\right)rw}{P^2(r^2 - a_1^2)^2 \tan\theta_0}. \quad \cdots \quad (9)$$

From (5) and (8),

$$H^2 = \frac{4}{3}\, \frac{\pi^2\left(a^2 + \frac{3}{32}\,d^2\right)w}{P^2(r_1^2 + a_1^2)^{\frac{3}{2}} \tan\theta_1}. \quad \cdots \quad (10)$$

When two deflectors are used, as described above, equations (9) and (10) take the form,

$$H^2 = \frac{8}{3}\, \frac{\pi^2 r\left(a^2 + \frac{3}{64}\,d^2\right)(P_1^2 w_2 + P_2^2 w_1)}{(r^2 - a_1^2)^2 P_1^2 P_2^2 \tan\theta_0}, \quad \cdots \quad (11)$$

and

$$H^2 = \frac{4}{3}\, \frac{\pi^2\left(a^2 + \frac{3}{32}\,d^2\right)(P_1^2 w_2 + P_2^2 w_1)}{(r_1^2 + a_1^2)^{\frac{3}{2}} P_1^2 P_2^2 \tan\theta_1}, \quad \cdots \quad (12)$$

where P_1 and P_2 are the periods of oscillation of the two deflectors respectively, $2a_1$ the mean of their effective lengths (supposed nearly equal), and w_1 and w_2 their masses in grammes.

Equations (9) to (12) give, of course, the same value for H if a_1 has been properly calculated. The value of $\frac{M}{w}$ is always calculated, as it gives an idea of the quality of steel used for the deflector. The results are given along with the values of H in tabular form below.

The values of H derived from equations (9) to (12) require correction, in the oscillation experiment, for arc of vibration, for virtual increase of inertia due to air moved, and for change of inertia, due to change of dimensions of the deflector, if the temperatures when the bar is measured and when it is vibrated are different. Neither of these produced a sensible error in the experiments, and hence they were neglected. There are besides a correction for the effect of variation of temperature during the experiment in altering the magnetic moment of the deflector, and a correction for the change of magnetic moment between the oscillation and deflection experiment, due to the deflector having its length in the direction of the magnetic meridian in the former, and at right angles to it in the latter experiment.

The magnets were found to change by $\frac{1}{21000}$ of their value per degree centigrade change of temperature; but as the change of temperature never exceeded two or three degrees, this correction was neglected.

The correction for induction, however, was found to be considerable in some cases, and the results tabulated below have all been corrected for that.

THE TEMPERATURE COEFFICIENT was obtained by placing the deflector behind the magnetometer-needle in such a position as to produce a deflection of 1000 scale-divisions, and the change of deflection produced by raising the temperature about 40° C. observed.

THE INDUCTION COEFFICIENT was determined by placing the deflector, surrounded by a magnetizing coil, near the magnetometer-needle, and observing the change of deflection produced by passing a known current through the coil. The arrangement for these measurements is illustrated in Pl. XI. fig. 3; and the results of a number of experiments on the effect of the length and hardness of the deflector on this correction are given in Table II., and are shown diagrammatically in the following curve.

Curve illustrating the effect of Ratio of Length to Diameter on the Inductive Coefficient.

Ratio of length to diameter.
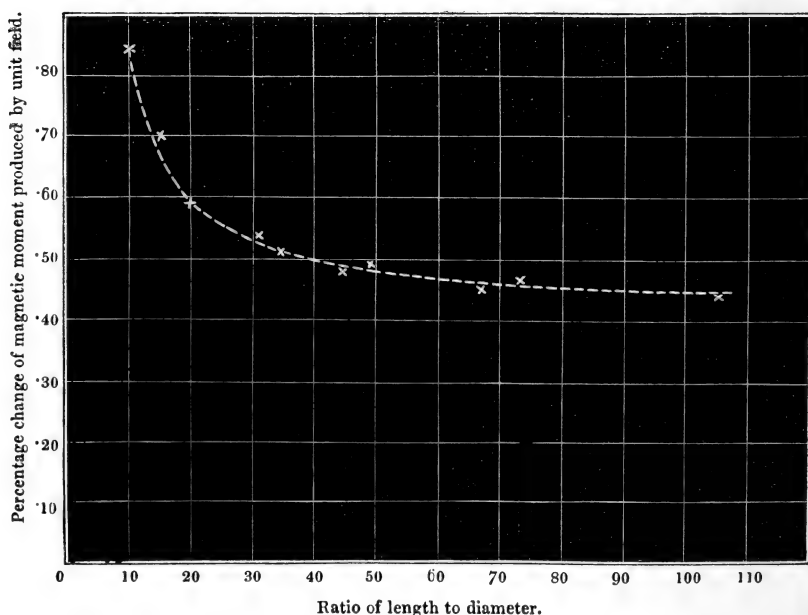
Referring to the figure, m is the magnetometer-needle ; C_0 and C_1 two coils, consisting of one layer of No. 30 B.W.G. silk-covered copper wire, wound in glass tubes about 5 millim. in external diameter ; C is a scale divided to millimetres, on which the deflection of the magnetometer-needle is read, in the manner described for the deflection-experiment above ; R is a box of resistance-coils, and G a current-galvanometer. The line D E represents a magnetic meridian, and A F a line passing through the centre of m and at right angles to D E.

The coil C_0 was placed with its axis parallel to A F, and its centre on the line D E. The coil C_1 was placed with its axis on the line A F, and at such a distance from m that a current passed in the proper directions through both coils produced no deflection. In making this adjustment a current, equal to about 30 times the greatest current subsequently used in the experiment, was passed through the coils.

The magnet to be tested was then introduced into one of the coils, adjusted to the proper position, and the deflection of m read. A current of such strength as to produce a field of about $\frac{1}{10}$ C.G.S. units intensity was then passed through the coils, and the change of deflection read. The current was then reversed, and the deflection again read. This operation was repeated with stronger and stronger currents until a field of from one to two units intensity was reached. The magnet was next introduced into the other coil, and a similar series of measurements taken. The results plotted on a sheet of section-paper show clearly that a field of considerably greater intensity than that used is required to permanently alter the magnetic moment of the magnets when they are hard-tempered.

The changes of deflection obtained when the magnet is in the coil C_0 are always a smaller fraction of the total deflection than they are when it is in the coil C_1. This is no doubt due to a change of magnetic distribution. The equations to the deflections in the two cases are :—

$$\theta = \frac{M}{H(r^2 + a_1^2)^{\frac{3}{2}}}$$

for the coil C_0, and

$$\theta_1 = \frac{2rM}{H(r^2 - a_1^2)^2}$$

for the coil C_1.

From these equations it is clear that either a change of M or of a_1 will affect the deflection, but that the effect of the change of a_1 is opposite in the two cases. The method of measurement

therefore allows both the change of moment M and the change of effective length $2a_1$ to be determined. When the change of moment only is required, this method has still an advantage in the fact that the effect of want of exact compensation between the two coils can be eliminated by means of the two measurements.

Sufficient sensibility is, for most purposes, obtained by using a deflection within the limits of the scale, but almost any degree of sensibility may be obtained by using an inferred zero. It is not advisable to place the magnets very near to m, because, if the tangent method be adopted, the compensation of the coils will not then be perfect unless m is always brought to its original zero position; and if this objection be got over by using a sine method, in which the whole apparatus, *including the magnetometer,* can be turned round a vertical axis, there still remains the objection that the effect of distribution becomes very pronounced. An inferred zero method therefore involves, when small magnets are being tested, a diminution, by artificial means, of the intensity of the field at m. This, however, cannot be pushed far, on account of the very inconvenient fluctuations of zero which then take place, due to changes of declination in the earth's field, combined with the small variations of intensity of " H " being superposed on a field, the whole strength of which is not large compared with these variations.

The results of these experiments, given in Table II., show that it is of great importance, so far as induction is concerned, that the length of the magnets should be at least forty times their diameter, and that they should be made as hard as possible. It appears that for the steel employed in the experiments, which was of the kind commonly called silver steel, a much stronger magnet is obtained with a blue than with a glass-hard temper*. The magnets were originally magnetized by placing them between the poles of a large Ruhmkorff magnet excited by 24 tray-cells. They were again magnetized by placing them between the poles of the same magnet

---

* *Note added October* 26, 1885.—Since this paper was in type I have received a copy of No. 14 of the 'Bulletins' of the United States Geological Survey, which is wholly devoted to a discussion of experiments on the "Physical Characteristics of the Iron-Carburets," by C. Barus and V. Strouhal. In this work a large number of interesting experiments on the effect of annealing specimens of this "silver steel," which had been previously tempered glass-hard, are quoted. Among other things the large increase of magnetic moment which is obtained by softening the steel, up to a certain point, is clearly brought out.—T. G.

excited by a dynamo having a low-resistance armature, and giving a potential of 100 volts. The relative strengths of the different magnets remained the same, and the strength only very slightly increased, thus showing that they were nearly magnetized to saturation.

The greatest trouble in the determination of the intensity of the earth's magnetic field arises out of the variations of the field itself—variations in declination causing changes of zero, and variations of intensity between different determinations causing apparent inaccuracy in the results.

This trouble was in the later measurements got over by means of a permanent magnetic vibrator, the period of vibration of which, at different times, gives a comparison of the intensity of the magnetic field at these times. In order to render the result of any one determination free from error due to diurnal variation, the period of the vibrator is taken at the beginning of the experiment, between the deflection and the oscillation experiment, and again at the end of the experiment. If these agree well and the results also agree well among themselves, the value found is considered reliable ; if not, the whole experiment is discarded. This vibrator has only lately been adopted, and hence the results up to those taken on June 11th are not corrected for diurnal variation. The results are tabulated in the order in which they were taken on each day ; and it will be observed that the earlier results are generally the smaller, this being due to diurnal variation. The last three results given in the Table are corrected to noon for diurnal variation.

It has been found impossible to get consistent results at all on several occasions, owing to extraordinary variations, and this was notably the case on the 1st of September. It is interesting to note how readily the vibrator shows extraordinary variations which take place suddenly. The observer has only to watch for sudden changes of amplitude. These changes of amplitude are sometimes extremely marked, the vibrator being almost stopped on some occasions, and afterwards gradually worked up to a large swing.

Table I. gives the results of the various determinations. The meanings of the numbers in the different columns are clearly indicated in the headings.

TABLE I.

Date, 1885.	Number of deflector.	Length of deflector, in centimetres.	Diameter of deflector, in centimetres.	Weight of deflector, in grammes.	Distance of centre of deflector from the magnetometer-needle, in cms. (East and west positions.)	Distance of centre of deflector from the magnetometer-needle, in cms. (North and south positions.)	Distance of the scale from the magneto-meter-mirror.	Effective length of the deflector.	Magnetic moment per gramme of the deflector.	Horizontal intensity in C.G.S. units.	Mean of each set of results.	Remarks.
May 27	1	8·03	0·25	3·054	32·06	28·75	108·7	6·91	44·9	·1520	......	
,, 27	2	8·05		3·063	,,	,,	,,	7·10	58·5	·1524	......	
,, 28	3	8·05		3·075	,,	,,	,,	6·31	54·1	·1521	·1522	
,, 29	4	8·05		3·067	,,	,,	,,	7·11	52·3	·1522		
June 5	5	4·00	0·25	1·526	30·00	25·125	,,	3·12	35·2	·1524	......	
,, 5	6	3·00		1·522	,,	,,	,,	3·72(?)	33·7	·1524	·1524	
,, 5	7	4·00		1·525	,,	,,	,,	2·33	31·7	·1527		
June 10	8	14·933	0·25	5·646	51·90	38·85	,,	13·22	55·8	·1527	......	
,, 11	9	15·030		5·727	,,	,,	,,	12·82	64·3	·1525	·1526	
,, 11	10	15·021		5·666	,,	,,	,,	13·58	54·5	·1527		
Aug. 21	11	10·01	0·2	2·318	35·00	30·00	128·9	9·14	71·0	·1526	......	Double deflector method.
,,	12	10·01		2·336	35·00	30·00			62·7			
,, 26	11	10·01		2·318	35·00	30·00	128·9	8·98	71·0	·1527	......	
,,	12	10·01		2·336					62·7			
,, 31	13	10·000		2·318	35·00	30·00	128·9	9·14	70·0	·1526	·1526*	
,,	14	10·005		2·336					61·8			

* Corrected to noon for diurnal variation.

TABLE II.—Showing the effect of Length and of Hardness on the Induction-Coefficient of Magnets.

Length of bar in centimetres.	Ratio of length to diameter.	Unit field.		Mean of numbers in columns 3 and 4.	Magnetic moment per gramme.	Remarks.
		Apparent percentage increase of moment for unit field: side-on position.	Apparent percentage increase of moment for unit field: end-on position.			
3	10	0·80	0·90	0·85	27	Glass hard
4	16	0·67	0·73	0·70	32	,,
4	16	0·67	0·70	0·69	35	,,
6	20	0·51	0 67	0·59	36	,,
7	31	0·51	0·58	0·54	39	,,
8	32	0·51	0·58	0·54	54	,,
8	32	0·51	0·58	0·54	52	,,
10	34	9·46	0·56	0·51	40	,,
10	44	0·40	0·56	0·48	43	,,
7	47	0·46	0·51	0·49	57	,,
10	50	0·44	0·58	0·51	67	,,
10	50	0·48	0·54	0·51	60	,,
10	50	0·46	0·55	0·51	53	,,
10	50	0·46	0·52	0·49	71	,,
10	50	0·46	0·56	0·51	60	,,
10	67	0·41	0·51	0·46	65	,,
7	73	0·41	0·50	0·47	64	,,
10	105	0·42	0·45	0·43	66	,,
10	34	0·47	0·53	0·50	41·5	Glass hard.
10	34	0·63	0·67	0·65	44·5	Yellow.
10	34	0·84	0·98	0·91	54·1	Blue.
10	48	0·32	0·40	0·36	45	Glass hard.
10	48	0·43	0·55	0·49	46	Yellow.
10	48	0·53	0·67	0·60	71	Blue.

LX. *The Periodic Law, as Illustrated by certain Physical Properties of Organic Compounds.*—Part II. *The Melting- and Boiling-points of the Halogen and Alkyl Compounds of the Hydrocarbon Radicals.* By THOMAS CARNELLEY, *D.Sc.,* Professor of Chemistry in University College, Dundee*.

IN the present series of papers my object is to determine whether the elements are in any way analogous to the hydrocarbon radicals of Organic Chemistry. For this purpose

* Communicated by the Author.

I have made a careful comparison of the physical properties (chiefly melting- and boiling-points) of a large number of both organic and inorganic compounds, and believe that I have been able to make out numerous and varied relationships between these properties.

My first paper (Phil. Mag. [5] xviii. p. 1) dealt with the melting- and boiling-points and heats of formation of the normal *halogen* compounds of the *elements*, and I showed that certain well-defined relationships existed as regards the above physical properties of these compounds. My second paper (ibid. [5] xx. p. 259) dealt in a similar manner with some of the physical properties of the normal *alkyl* compounds of the *elements*, which were shown to exhibit exactly the same relationships as those of the corresponding halogen compounds; proving, therefore, that the function of the alkyl radicals— methyl CH_3, ethyl C_2H_5, propyl C_3H_7, &c.—was exactly analogous to that of the halogen elements—chlorine, bromine, and iodine.

In the present paper I wish to show that the normal halogen and alkyl compounds of the hydrocarbon radicals exhibit relationships similar to those of the corresponding compounds of the elements, and therefore that the elements and hydrocarbon radicals are analogous and have the same function in their several compounds. In a fourth and final paper I intend to take a general review of the whole question, and to draw certain conclusions as to the nature of the chemical elements and of the Periodic Law.

The following table contains the experimental data, with the authorities, which have been used in drawing the conclusions given below. For the purpose of avoiding minus signs all temperatures are reckoned from the absolute zero (-273). The following abbreviations are used :—Me = methyl, CH_3 ; Et = ethyl, C_2H_5 ; Pr^{α} = normal propyl, $CH_3 . CH_2 . CH_2$— ; Pr^{β} = isopropyl $(CH_3)_2CH$—.

TABLE I.—Experimental Data.

	Constitution.	Melting- and Boiling- point.	Authority.
Chlorides :—			
Methyl chloride	$CH_3 . Cl$....................	b.p. 249	Regnault.
Ethyl ,, ...	$CH_3 . CH_2 . Cl$	b.p. 285	,,
Propyl ,, ...	$CH_3 . CH_2 . CH_2 . Cl$ ...	b.p. 319	Linnemann.
,, ,, ...	$CH_3 . CHCl . CH_3$	b.p. 310	,,
Butyl ,, ...	$CH_3 . (CH_2)_3 . Cl$	b.p. 351	,,
,, ,, ...	$CHMe_2 . CH_2 . Cl$	b.p. 342	,,
,, ,, ...	$CMe_3 . Cl$	b.p. 324	Perkin.
Amyl ,, ...	$CH_3 . (CH_2)_4 . Cl$	b.p. 380	Lieben and Rossi.
,, ,, ...	$CHEt_2 . Cl$..................	b.p. 377	Wagner and Saytzeff.
,, ,, ...	$CHMePr\alpha . Cl$	b.p. 377	,, ,,
,, ,, ...	$CHMe_2 . CH_2 . CH_2 . Cl$..	b.p. 374	Carius and Fries.
,, ,, ...	$CHMePr\beta . Cl$	b.p. 360	Butlerow.
,, ,, ...	$CMe_2Et . Cl$	b.p. 359	Perkin.
Hexyl ,, ...	$CH_3 . (CH_2)_5 . Cl$	b.p. 406	Lieben and Janecek.
,, ,, ...	$Me . (CH_2)_3 . CHCl . Me$..	b.p. 397	Schorlemmer.
,, ,, ...	$CHMe_2 . CMe_2 . Cl$	b.p. 387	Friedel and Silva.
,, ,, ...	,, ,, ...	m.p. 271	Kaschirsky.
Heptyl ,, ...	$CH_3 . (CH_2)_6 . Cl$	b.p. 432	Cross.
,, ,, ...	$CHMe_2 . (CH_2)_4 . Cl (?)$..	b.p. 423	
,, ,, ...	$CMe_3 . CMe_2 . Cl$	m.p. 409	Butlerow.
,, ,, ...	$Pr\beta . (CH_2)_2 . CHMe . Cl$	b.p. 409	Rohu.
Octyl ,, ...	$CH_3 . (CH_2)_7 . Cl$	b.p. 456	Perkin.
,, ,, ...	$C_6H_{13} . CHMe . Cl$	b.p. 448	Schorlemmer.
,, ,, ...	$C_5H_{11} . CHEt . Cl$........	b.p. 448	,,
,, ,, ...	$C_8H_{17}Cl$	b.p. 438	,,
,, ,, ...	$CEt_2Pr\alpha . Cl$	b.p. 428	Butlerow.
,, ,, ...	$C_8H_{17}Cl$	b.p 421	
Methylene dichloride ...	CH_2Cl_2	b.p. 315	Thorpe.
Ethylene ,, ...	$CH_2Cl . CH_2Cl$	b.p. 357	,,
Ethylidene ,, ...	$CH_3 . CHCl_2$	b.p. 333	,,
Propylene ,, ...	$Cl . (CH_2)_2 . Cl$	b.p. 392	Reboul.
,, ,, ...	$CH_3 . CHCl . CH_2Cl$ ...	b.p. 370	Linnemann.
,, ,, ...	$CH_3 . CH_2 . CHCl_2$	b.p. 359	Reboul.
,, ,, ...	$CH_3 . CCl_2 . CH_3$	b.p. 343	Perkin.
Butylene ,, ...	$C_4H_8Cl_2$	b.p. 405	Wurtz.
,, ,, ...		b.p. 395	Kopp.
,, ,, ...	$CHMe_2 . CHCl_2$	b.p. 377	Œconimides.
,, ,, ...	$CH_3 . CCl_2 . CH_3 . CH_3$..	b.p. 369	Bruylants.
Amylene ,, ...	$C_5H_{10}Cl_2$	b.p. 430	Buff.
,, ,, ...	$Pr\alpha . CCl_2 . Me$	b p. 418	Friedel.
,, ,, ...	$CHMe_2 . CH_2 . CHCl_2$ ...	b.p. 402	Bruylants.
Hexylene ,, ...	$CMe_2Cl . CMe_2Cl$	m.p. 433	Friedel and Silva.
,, ,, ...	$C_6H_{12}Cl_2$	b.p. 455	Pelouze and Cahours.
,, ,, ...	,,	b.p. 448	Wurtz.
,, ,, ...		b.p. 437	Henry.
Heptylene ,, ...	$C_7H_{14}Cl_2$	b.p. 463	Schorlemmer.
,, ,, ...	$Pr\alpha . CCl_2 . Pr\alpha$	b.p. 454	Tawildarow.
Octylene ,, ...	$C_8H_{16}Cl_2$	b.p. 508	Thorpe and Young.
,, ,, ...		b.p. 481	Nieson.
,, ,, ...	$C_6H_{13} . CCl_2 . Me$	b.p. 470	*Annalen,* cvi. 271.

TABLE I. (*continued*).

	Constitution.	Melting- and Boiling- point.	Authority.
Trichlor-methane	$CHCl_3$ .... $\{$	b.p. 334	Thorpe.
		m.p. 203	Berthelot.
Trichlor-ethane............	$CH_2Cl'.CHCl_2$	b.p. 387	Staedel.
,, ,, ...	$CH_3.CCl_3$	b.p. 347	,,
Trichlor-propane	$CH_2Cl.CHCl.CH_2Cl...$	b.p. 431	Perkin.
,, ,, ...	$CH_2Cl.CH_2.CHCl_2$ ...	b.p. 420	Romburgh.
,, ,, ...	$CH_3.CHCl.CHCl_2...$	b.p. 413	Friedel and Silva.
,, ,, ...	$CH_3.CCl_2.CH_2Cl$	b.p. 398	,,
Trichlor-pentane	$C_5H_9Cl_3$	b.p. 460	Buff.
,, ,, ...		b.p. 448	Bauer.
Trichlor-hexane	$C_6H_{11}Cl_3$	b.p. 490	Pelouze and Cahours.
Tetrachlor-methane......	CCl_4 .... $\{$	b.p. 350	Thorpe.
		m.p. 248	Regnault.
Tetrachlor-ethane.........	$CHCl_2.CHCl_2$	b.p. 420	Staedel.
,, ,, ...	$CH_2Cl.CCl_3$	b.p. 403	,,
Tetrachlor-propane	$C_3H_4Cl_4$ .... $\{$	m.p. 418	$\}$ Berthelot.
		b.p. 473	
,, ,, ...		b.p. 453	Romburgh.
,, ,, ...	$CH_2Cl.CCl_2.CH_2Cl$ ...	b.p. 437	Henry.
,, ,, ...	$C_3H_4Cl_4$	b.p. 426	Borsche.
,, ,, ...		m.p. 451	Schorlemmer.
Tetrachlor-butane	$C_4H_6Cl_4$	Liquid.	Thurnlackl.
,, ,, ...		m.p. 346	*Bull. Chim.* **xxxiv.** 195.
Tetrachlor-pentane	$C_5H_8Cl_4$	b.p. 508	Bauer.
Trichlor-ethylene	$CCl_2:CHCl$	b.p. 360	Paterno.
Trichlor-propylene, β ...	$C_3H_5Cl_3$	b.p. 415	Pfeffer and Fittig.
,, ,, α ...	$C_3H_3Cl_3$	b.p. 388	Borsche.
Trichlor-amylene	$C_5H_7Cl_3$	b.p. 473	Bauer.
Dichlor-acetylene	$CCl \equiv CCl.$ .... $\{$	b.p. 460	$\}$ Watts Dict. i. 768.
		m.p. 460	
Dichlor-allylene	$CH_2:C:CCl_2$	b.p. 351	Pinner.
Chlornicene	C_5H_5Cl	b.p. 566	St. Evre.
Bromides:—			
Methyl bromide	$CH_3.Br$	b.p. 278	Perkin.
Ethyl ,, ...	$CH_3.CH_2.Br$	b.p. 312	,,
Propyl ,, ...	$CH_3.CH_2.CH_2.Br$ ...	b.p. 344	,,
,, ,, ...	$CH_3.CHBr.CH_3$	b.p. 334	Linnemann.
Butyl ,, ...	$CH_3.(CH_2)_3.Br$	b.p. 373	,,
,, ,, ...	$CHMe_2.CH_2.Br$	b.p. 365	,,
,, ,, ...	$CMe_3.Br$	b.p. 344	Perkin.
Amyl ,, ...	$CH_3.(CH_2)_4.Br$	b.p. 402	Lieben and Rossi.
,, ,, ...	$CHMe_2.(CH_2)_2.Br$......	b.p. 393	Perkin.
,, ,, ...	$CHMe_2.CHMe.Br$......	b.p. 386	Wurtz.
,, ,, ...	$CMe_2Et.Br$	b.p. 382	Wischnegradsky.
Hexyl ,, ...	$CH_3.(CH_2)_5.Br$	b.p. 428	Lieben.
,, ,, ...	$C_4H_9.CHMe.Br$........	b.p. 417	Schorlemmer.
,, ,, ...	$CHMePr\alpha.CH_2Br$	b.p. 416	*Monatschrift,* iv. 34.
Heptyl ,, ...	$CH_3.(CH_2)_6.Br$	b.p. 452	Cross.
,, ,, ...	$CH_3.(CH_2)_4.CHMe.Br$	b.p. 439	Venables.
,, ,, ...	$CMe_3.CMe_2.Br$	m.p. 425	Kaschirsky.

TABLE I. (*continued*).

	Constitution.	Melting- and Boiling- point.	Authority.
Octyl bromide	$CH_3 . (CH_2)_7 . Br$	b.p. 476	Perkin.
,, ,, (sec.) ...	$C_8H_{17} . Br$	b.p. 461	Lachowicz.
Methylene dibromide ...	CH_2Br_2 .... {	b.p. 370	Perkin. }
		m.p.b. 261	Henry. }
Ethylene ,, ...	$CH_2Br . CH_2Br$ ...... {	b.p. 405	} Thorpe.
		m.p. 282	
Ethylidene ,, ...	$CH_3 . CHBr_2$	b.p. 382	Perkin.
Propylene ,, ...	$Br . (CH_2)_3 . Br$...........	b.p. 438	Freund.
,, ,, ...	$CH_3 . CHBr . CH_2Br$ ...	b.p. 415	Perkin.
,, ,, ...	$CH_3 . CH_2 . CHBr_2$	b.p. 405	Reboul.
,, ,, ...	$CH_3 . CBr_2 . CH_3$	b.p. 387	,,
Butylene ,, ...	$CHMeBr . CHMeBr$ ...	b.p. 439	Wurtz.
,, ,, ...	$CHEtBr . CH_2Br$	b.p. 431	,,
,, ,, ...	$CMe_2Br . CH_2Br$	b.p. 422	Perkin.
Amylene ,, ...	$C_5H_{10}Br_2$	b.p. 459	Thorpe and Young.
,, ,, ...	$CHEtBr . CHMeBr$	b.p. 451	Wagner.
,, ,, ...	$CHMe_2 . CHBr . CH_2Br$	b.p. 448	Bruylants.
Hexylene ,, ...	$C_5H_{11} . CHBr_2$	b.p. 483	*Annalen,* cxxiv. 293.
,, ,, ...	$C_6H_{12} . Br_2$	b.p. 458	Helbing.
,, ,, ...	$CMe_2Br . CMe_2Br$.........	m.p. 442	Rizza.
,, ,, ...	$C_6H_{12}Br_2$	m.p. 413	Eltekoff.
,, ,, ...	$Pr\beta . CHBr . CHMe . Br$	m.p. 412	,,
Octylene ,, ...	$C_8H_{16}Br_2$	b.p. 473 *d*	Nieson.
Tribrom-methane	$CHBr_3$ .... {	b.p. 424	Thorpe. }
		m.p. 281	Perkin. }
Tribrom-ethane	$CH_2Br . CHBr_2$	b.p. 462	Perkin.
,, ,, ...	$CH_3 . CBr_3$	b.p. 461	Denzel.
Tribrom-propane	$CH_2Br . CHBr . CH_2Br$ {	b.p. 493	} Henry.
		m.p. 289	
,, ,, ...	$CH_3 . CHBr . CHBr_2$ ...	b.p. 473	Reboul.
,, ,, ...	$CH_3 . CBr_2 . CH_2Br$	b.p. 463	,,
Tribrom-butane	$Me_2CBr . CHBr_2$	b.p. 489	Linnemann.
,, ,, ...	$C_4H_7Br_3$	b.p. 485	Caventou.
Tetrabrom-methane	CBr_4... .... {	b.p. 462	Bolas and Groves.
		m.p. 364	,,
Tetrabrom-ethane.........	$CH_2Br . CBr_3$ .... {	b.p. 493	Kessel.
		m.p. 327	Burgoin.
,, ,, ...	$CHBr_2 . CHBr_2$......... {	b.p. 482	Tawildarow.
		m.p.b. 249	Anschütz.
Tetrabrom-propane	$CH_2Br . CBr_2 . CH_2Br$ ...	m.p. 468	Hartenstein.
,, ,, ...	$C_3H_5Br_3$ .... {	m.p. 342	} *Annalen,* cxxxvi. 64.
		b.p. 513 *d*	
,, ,, ...	$CHBr_2 . CHBr . CH_2Br$..	b.p. 524	Reboul.
,, ,, ...	$CH_3 . CBr_2 . CHBr_2$......	b.p. 503	Oppenheim.
Tetrabrom-butane.........	$C_4H_6Br_4$..............	m.p. 389	Caventou.
,, ,, ...	$CHBr_2 . CBr_2 . CH_2Me$..	m.p. 387	Prunier.
,, ,, ...	$C_4H_6Br_4$	m.p. 372	*Annalen,* clxxii. 291.
Tetrabrom-pentane	$CMe_2Br . CBr_2 . CH_2Br$..	m.p. 388	Hoffmann.
,, ,, ...	$Pr\alpha . CBr_2 . CHBr_2$	b.p. 548	Bruylants.
,, ,, ...	$Pr\beta . CBr_2 . CHBr_2$	b.p. 548	,,
Tetrabrom-hexane	$C_6H_{10}Br_4$	m.p. 415	Bouchardat.
,, ,, ...	,, ...	m.p. 393	*Zeit. Chem.* 1871.

<div align="center">TABLE I. <i>(continued)</i>.</div>

	Constitution.	Melting- and Boiling- point.	Authority.
Tetrabrom-hexane	$C_6H_{10}Br_4$ .... $\Big\{$	m.p. 385 b.p. 591	$\Big\}$ *Annalen,* cxxxix. 251.
,, ,, ...	$(CH_2)_2(CHBr . CH_2Br)_2$	m.p. 336	Wagner.
Tribrom-ethylene	$CHBr : CBr_2$...............	b.p. 435	Anschütz.
Tribrom-propylene	$CHBr : CBr . CH_2Br$ ...	non-vol.	Henry.
,, ,, ...	$C_3H_3Br_3$	b.p. 457	Oppenheim.
Dibrom-diallyl	$C_3H_4Br . C_3H_4Br$	b.p. 483	Henry.
Brom-diallylene	C_6H_7Br	b.p. 423	,,
Caprylidene bromide ...	$C_8H_{11}Br$.....................	b.p. 477	*Annalen,* cxlii. 300.
Iodides :—			
Methyl iodide	CH_3I	b.p. 315	Perkin.
Ethyl ,, ...	$CH_3 . CH_2I$	b.p. 345	Linnemann.
Propyl ,, ...	$CH_3 . CH_2 . CH_2I$	b.p. 375	,,
,, ,,	$CH_3 . CHI . CH_3$	b.p. 362	Perkin.
Butyl iodide	$CH_3 . (CH_2)_3 . I$	b.p. 403	Linnemann.
,, ,, ...	$CHMe_2 . CH_2I$	b.p. 393	Perkin.
,, ,, ...	$CHMeEt . I$	b.p. 392	Lieben.
,, ,, ...	$CMe_3 . I$...............	b.p. 373	Puchot.
Amyl ,, ...	$CH_3 . (CH_2)_4 . I$	b.p. 429	Lieben and Rossi.
,, ,, ...	$CHMe_2 . (CH_2)_2 . I$	b.p. 421	Perkin.
,, ,, ...	$CH_3 . (CH_2)_2 . CHI . CH_3$	b.p. 419	Wurtz.
,, ,, ...	$CHEt_2 . I$	b.p. 418	Wagner.
,, ,, ...	$CHMe_2 . CHI . CH_3$	b.p. 411	Wischnegradsky.
,, ,, ...	$CMe_2Et . I$...............	b.p. 401	,,
Hexyl ,, ...	$CH_3 . (CH_2)_5 . I$	b.p. 454	Lieben.
,, ,, ...	$CHMe_2 . (CH_2)_3 . I$	b.p. 446	Pelouze.
,, ,, ...	$CH_3 . (CH_2)_3 . CHI . CH_3$	b.p. 440	Wanklyn.
,, ,, ...	$CHEtPr\alpha . I$	b.p. 438	Connick.
,, ,, ...	$CMe_3 . CHI . CH_3$	b.p. 415	*Jahresb.* 1873.
,, ,, ...	$CMe_2Pr\alpha . I$	b.p. 415	*Annalen,* cxcv. 254.
,, ,, ...	$CMe_2Pr\beta . I$ .... $\Big\{$	b.p. 414 s. 273	$\Big\}$ Kaschirsky.
Heptyl ,, ...	$CH_3 . (CH_2)_6 . I$............	b.p. 474	Cross.
,, ,, ...	$CHPr\alpha_2 . I$...............	b.p. 458	*Jahresb.* 1869.
,, ,, ...	$Pr\beta . (CH_2)_2 . CHI . CH_3$	b.p. 443	Rohu.
,, ,, ...	$CMeEtPr\beta . I$...............	b.p. 419	Kaschirsky.
,, ,, ...	$CMe_3 . CMe_2 . I$...............	b.p. 414	Butlerow.
Octyl ,, ...	$CHMe_2 . (CH_2)_5 . I$	b.p. 494	Zincke.
,, ,, ...	$C_6H_{13} . CHI . CH_3$	b.p. 484	Bouis.
Methylene diiodide	CH_2I_2..................... $\Big\{$	b.p. 453 m.p. 277	$\Big\}$ Hofmann.
Ethylene ,, ...	$CH_2I . CH_2I$	m.p. 355	Aronstein.
Ethylidene ,, ...	$CH_3 . CHI_2$	b.p. 453	Plimpton.
Propylene ,, ...	$CH_2I . CH_2 . CH_2I$	b.p. 500 *d*	Freund.
,, ,, ...	$C_3H_6I_2$	b.p. 421 *d*	Semenoff.
Triiodo-methane	CHI_3	m.p. 392	Serullas.
Tetraiodo-methane	CI_4..................... $\Big\{$	m.p. 420 b.p. 620	$\Big\}$ Calculated. Phil.Mag.[5]xviii.17.
Tetraiodo-hexane	$(CH_2)_2(CHI . CH_2I)_2$ ...	m.p. a. 373	*Annalen,* c. 363.
Triiodo-propylene.........	$CI_2 : CI . CH_3$	m.p. 337	Liebermann.
,, ,, ...	$CHI : CI . CH_2I$	m.p. 314	Henry.

Table I. (*continued*).

	Constitution.	Melting- and Boiling-point.	Authority.
Alkyl compounds (Hydrocarbons):—			
Propane....................	Normal	b.p. 245	Lefebvre.
Butane	,, ...	b.p. 274	Schorlemmer.
	$CHMe_3$	b.p. 256	Butlerow.
Pentane	Normal	b.p. 311	Schorlemmer.
,, ...	$CHMe_2 . CH_2 . Me$	b.p. 303	Pelouze.
,, ...	CMe_4 .... {	b.p. 282 s. 253	} Lwow.
Hexane	Normal	b.p. 344	Schorlemmer.
, ...	$CHMe_2 . (CH_2)_2 . Me$ ...	b.p. 335	,,
,, ...	$CHMeEt_2$	b.p. 337	Wislicenus.
,, ...	$CHMe_2 . CHMe_2$	b.p. 331	Schorlemmer.
,, ...	CMe_3Et	b.p. 318	Butlerow.
Heptane....................	Normal	b.p. 371	Thorpe.
,, ...	$CHEt_3$	b.p. 370	Ladenburg.
,, ...	$CHMeEtPr\alpha$	b.p. 364	Just.
,, ...	$CHMe_2 . (CH_2)_2 . Et$.....	b.p. 363	Thorpe.
,, ...	CMe_2Et_2	b.p. 360	Friedel.
Octane	Normal	b.p. 398	Thorpe.
,, ...	$CHMe_2 . (CH_2)_2 . CHMe_2$	b.p. 381	Williams.
,, ...	$CMe_3 . CMe_3$ .... {	b.p. 379 m.p. 369	} Lwow.
Nonane	Normal .... {	b.p. 422 m.p. 222	} Krafft.
,, ...	$CHMe_2 . (CH_2)_3 . CHMe_2$	b.p. 405	Wurtz.
,, ...	$Pr\beta . CH_2 . CHMePr\beta$ ...	b.p. 403	Silva.
Decane	Normal .... {	b.p. 446 m.p. 241	} Krafft.
Undecane	,, ... {	b.p. 468 m.p. 247	} ,,
Amylene	$CMe_2 : CHMe$	b.p. 309	Flawitzky.
Hexylene	$CMe_2 : CMe_2$..............	b.p. 346	Rizza.
,, ...	$CHMe : CMeEt$.............	b.p. 343	Jawein.
,, ...	$CMe_2 : CHEt$..............	b.p. 339	,,
Heptylene	$CMe_2 : CMeEt$	b.p. 366	Kaschirsky.
,, ...	$CHMe_2 . CH : CMe_2$......	b.p. 355	Markownikow.
,, ...	$CMe_3 . CMe : CH_2$........	b.p. 352	Eltekoff.
Octylene	$C_5H_7Me_3$	b.p. 395	Williams.
,, ...	$CHPr\beta : CHPr\beta$	b.p. 391	Fossek.
,, ...	$CMe_2 : CH . CMe_3$........	b.p. 376	Butlerow.
Methylethyl-acetylene ...	$CMe : CEt$....................	b.p. 324	Eltekoff.
Valerylene....................	$CMe_2 : C : CH_2$	b.p. 318	Reboul.
Isopropyl-acetylene	$CH : CPr\beta$	b.p. 301	Flawitzky.
Valylene....................	$CH_2 : CMe . C : CH$......	b.p. 323	Reboul.
Hexine	$CMe : CPr\alpha$	b.p. 355	Hecht.
Heptine	$CHMe : C : CHPr$........	b.p. 376	Tilden.
,, ...	$CMe_2 : C : CMe_2$	b.p. 343	Henry.

By the normal halogen or alkyl compounds of the hydro-carbon radicals we mean the compounds formed by the following radicals with the halogens chlorine, bromine, and iodine, or with methyl, ethyl, propyl, &c. ; viz. :—

	Series 1.	Series 2.	Series 3.	Series 4.	Series 5.	
Group I	......	......	$(C_3H)X_1$	$(C_4H_3)X_1$	$(C_5H_5)X_1$	
„ II. ...	......	$(C_2)X_2$	$(C_3H_2)X_2$	$(C_4H_4)X_2$	$(C_5H_6)X_2$	
„ III. ...	......	$(C_2H)X_3$	$(C_3H_3)X_3$	$(C_4H_5)X_3$	$(C_5H_7)X_3$	Series 6, 7, 8, &c. being similarly constructed.
„ IV. ...	CX_4	$(C_2H_2)X_4$	$(C_3H_4)X_4$	$(C_4H_6)X_4$	$(C_5H_8)X_4$	
„ V. ...	$(CH)X_3$	$(C_2H_3)X_3$	$(C_3H_5)X_3$	$(C_4H_7)X_3$	$(C_5H_9)X_3$	
„ VI. ...	$(CH_2)X_2$	$(C_2H_4)X_2$	$(C_3H_6)X_2$	$(C_4H_8)X_2$	$(C_5H_{10})X_2$	
„ VII. ...	$(CH_3)X_1$	$(C_2H_5)X_1$	$(C_3H_7)X_1$	$(C_4H_9)X$	$(C_5H_{11})X_1$	

In the above, $X = Cl$, Br, I, CH_3, C_2H_5, or C_3H_7, &c.

The above series, of course, might be considerably extended; but I have not thought it necessary to carry my investigations beyond the 8th series for the halogen compounds, nor beyond the 5th series for the alkyl compounds*.

When there are several isomeric modifications of the same empirical formula, only those which are strictly analogous should be compared; thus, normal compounds should be compared with normal, and iso-compounds with iso-, &c. In some instances, however, this is not possible, owing to the data being incomplete, or to the constitution being unknown, or when the compounds belonging to *different groups* of the *same series* are to be compared; in this case the mean of the melting- or boiling-points of the several isomeric compounds is employed. As a general rule, however, the same results are obtained, no matter whether we use the mean melting- or boiling-point for all the isomeric compounds, or whether we compare only those compounds which are strictly analogous.

Now the same general rule that we have already shown (ibid. xviii. p. 2) to hold good as regards the corresponding compounds of the elements also holds in the case of the above hydrocarbon radicals; for in whatever way we may arrange the melting- or boiling-points of their normal halogen or alkyl compounds, provided only that we arrange them systematically, we always find that certain definite and regular relations may be traced between them. The following are examples of such relations :—

RELATION 1. *If the above hydrocarbon radicals be arranged in the order of their atomic weights, then the melting-points and boiling-points of both their halogen and alkyl compounds rise and fall periodically.*

This periodicity is such that the values increase from the

* The methide curve in the diagram which accompanies the paper has, however, been completed to the end of the eighth series.

first (monad) up to the fourth or middle (tetrad) member of each series, and then diminish to the seventh (monad) or last member (see Table II.*).

This periodicity is not *exactly* the same as that in the case of the corresponding compounds of the elements ; I shall not, however, discuss this point at present, but defer it to my next communication.

TABLE II.—Illustrating Relations 1 and 2.

HALOGEN COMPOUNDS.	CHLORIDES.		BROMIDES.		IODIDES.	
	M.P.	B.P.	M.P.	B.P.	M.P.	B.P.
......	......	......	......	......	......	......
......	......	......	......	......	......	......
......						
C^{iv} ...	248	350	364	462	420	620
$(CH)^{iii}$	203	334	281	424	392	......
$(CH_2)^{ii}$	Liquid.	315	b. 261	370	277	453
$(CH_3)^{i}$	Liquid.	249	Liquid.	278	Liquid.	315
......						
C_2^{ii} ...	460[1](?)	460[1](?)	......	......	......	......
$(C_2H)^{iii}$	Liquid.	360	Liquid.	435	......	......
$(C_2H_2)^{iv}$	Liquid.	411	327	488	......	......
$(C_2H_3)^{iii}$	Liquid.	367	Liquid.	462	......	......
$(C_2H_4)^{ii}$	Liquid.	345	......	393	355	453 d.
$(C_2H_5)^{i}$	Liquid.	285	Liquid.	312	Liquid.	345
$(C_3H)^{i}$	......	......	......	......	......	......
$(C_3H_2)^{ii}$	Liquid.	351	......	......	......	......
$(C_3H_3)^{iii}$	Liquid.	402	Liquid.	457	326	......
$(C_3H_4)^{iv}$	434	447	405	513	......	......
$(C_3H_5)^{iii}$	b. 263	415	289	476	......	......
$(C_3H_6)^{ii}$	Liquid.	366	Liquid.	411	Liquid.	460
$(C_3H_7)^{i}$	Liquid.	315	Liquid.	339	Liquid.	368
$(C_4H_3)^{i}$	......	......	......	......	......	......
$(C_4H_4)^{ii}$	......	......	......	......	......	......
$(C_4H_5)^{iii}$	......	......	......	......	......	......
$(C_4H_6)^{iv}$	346	......	383	......	......	......
$(C_4H_7)^{iii}$	......	......	......	487	......	......
$(C_4H_8)^{ii}$	Liquid.	386	Liquid.	431	......	......
$(C_4H_9)^{i}$	Liquid.	339	Liquid.	361	Liquid.	390
$(C_5H_5)^{i}$	Liquid.	566(?)[2]	......	......	......	......
$(C_5H_6)^{ii}$	Liquid.	419	......	......	......	......
$(C_5H_7)^{iii}$	Liquid.	473	......	......	......	......
$(C_5H_8)^{iv}$	Liquid.	508	388	548	......	......
$(C_5H_9)^{iii}$	Liquid.	454	Solid.	......	......	......
$(C_5H_{10})^{ii}$	Liquid.	417	Liquid.	453	......	......
$(C_5H_{11})^{i}$	Liquid.	371	Liquid.	391	Liquid.	416

* The periodicity is rendered still more evident by the curves for the methides, chlorides, and bromides shown in the diagram (p. 514).

TABLE II. (*continued*).—Illustrating Relations 1 and 2.

		METHIDES.		ETHIDES.		NORMAL PROPIDES.	
		M.P.	B.P.	M.P.	B.P.	M.P.	B.P.
	......	......	......	......	......	......	......
	......	......	......	......	......	......	......
	......	......	......	......	......	......	......
	C^{iv} ... {	Solidifies 253	} 282	......	......	......	......
	$(CH)^{iii}$	Liquid.	256	Liquid.	370	......	......
	$(CH_2)^{ii}$	Liquid.	245	Liquid.	311	......	......
	$(CH_3)^{i}$	......	Gas.	Liquid.	245	Liquid.	371
						Liquid.	274
	......	......	......	......	......	......	......
	C_2^{ii} ...	......	......	......	......	......	......
	$(C_2H)^{iii}$	Liquid.	309	......	......	......	......
	$(C_2H_2)^{iv}$	Liquid.	325	......	......	......	......
	$(C_2H_3)^{iii}$	Liquid.	293	......	......	......	......
	$(C_2H_4)^{ii}$	Liquid.	265	Liquid.	341	Liquid.	398
	$(C_2H_5)^{i}$	Liquid.	245	Liquid.	274	Liquid.	311
ALKYL COMPOUNDS.	$(C_3H)^{i}$	......	......	......	......	......	......
	$(C_3H_2)^{ii}$	Liquid.	314	......	......	......	......
	$(C_3H_3)^{iii}$	Liquid.	343	......	......	......	......
	$(C_3H_4)^{iv}$	Liquid.	360	......	......	......	......
	$(C_3H_5)^{iii}$	Liquid.	330	......	......	......	......
	$(C_3H_6)^{ii}$	Liquid.	299	Liquid.	366	222	422
	$(C_3H_7)^{i}$	Liquid.	265	Liquid.	307	Liquid.	340
	$(C_4H_3)^{i}$	Liquid.	323	......	......	......	......
	$(C_4H_4)^{ii}$	Liquid.	355	......	......	......	......
	$(C_4H_5)^{iii}$	Liquid.	358	......	......	......	......
	$(C_4H_6)^{iv}$	369	380	......	......	......	......
	$(C_4H_7)^{iii}$	Liquid.	364	......	.. ...	......	......
	$(C_4H_8)^{ii}$	Liquid.	333	Liquid.	398	241	446
	$(C_4H_9)^{i}$	Liquid.	299	Liquid.	333	Liquid.	366
	$(C_5H_5)^{i}$	......	......	......	......	......	......
	$(C_5H_6)^{ii}$	Liquid.	360	......	......	......	......
	$(C_5H_7)^{iii}$	Liquid.	387	......	......	......	......
	$(C_5H_8)^{iv}$	Liquid.	404	......	......	......	......
	$(C_5H_9)^{iii}$	Liquid.	381	......	......	.. ...	......
	$(C_5H_{10})^{ii}$	Liquid.	365	222	422	247	468
	$(C_5H_{11})^{i}$	Liquid.	333	Liquid.	365	Liquid.	398

N.B.—In the above table the mean value is given when there are several isomers having the same empirical composition. Sometimes, however, in the case of the melting-points, there are several pairs or triplets of isomeric substances of which the melting-point of one only is known, the others being liquid; a mean number is therefore impossible; in this case the known melting-point is given.

[1] This is the mean of 448°–473°, which are the temperatures given in Watts's Dictionary (i. p. 768) as those between which protochloride of carbon melts and boils. Chlorine does not act upon this compound even in sunshine. It is most probably a polymer $(C_2Cl_2)_n$. Berthelot in fact regards it as $C_{10}Cl_{10}$. Its vapour-density, however, does not appear to have been determined.

[2] This is the boiling-point of chlornicene, as given by St. Evre (*Jahresbericht*, i. p. 530). This substance, if a definite compound, is probably a polymer $(C_5H_5Cl)_n$.

Relation 2. *The melting-points and boiling-points of either the halogen or alkyl compounds of any hydrocarbon radical increase as we pass from the chloride to the bromide and thence to the iodide; or from the methide to the ethide, and thence to the propide, &c.* (See Tables II. and III.)

Table III.—Illustrating Relations 2 and 3.

Halogen compounds.	Chlorides.		Bromides.		Iodides.	
	M.P.	B.P.	M.P.	B.P.	M.P.	B.P.
CH_3 ...	Liquid.	249	Liquid.	278	Liquid.	315
C_2H_5 ...	Liquid.	285	Liquid.	312	Liquid.	345
C_3H_7 ...	Liquid.	319	Liquid.	344	Liquid.	375
C_4H_9 ...	Liquid.	351	Liquid.	373	Liquid.	403
C_5H_{11} ...	Liquid.	380	Liquid.	402	Liquid.	429
C_6H_{13} ...	Liquid.	406	Liquid.	428	Liquid.	454
C_7H_{15} ...	Liquid.	432	Liquid.	452	Liquid.	474
C_8H_{17} ...	Liquid.	456	Liquid.	476	Liquid.	a. 494

Normal primary halides of Group VII. $CH_3.(CH_2)_n.X.$

Alkyl compounds.	Methides.		Ethides.		α-Propides.	
CH_3 ...	......	Gas.	......	245	Liquid.	274
C_2H_5 ...	......	245	Liquid.	274	Liquid.	311
C_3H_7 ...	Liquid.	274	Liquid.	311	Liquid.	344
C_4H_9 ...	Liquid.	311	Liquid.	344	Liquid.	371
C_5H_{11} ...	Liquid.	344	Liquid.	371	Liquid.	398

Normal primary alkides of Group VII. $CH_3.(CH_2)_n.X.$

	Methides.		Ethides.		Propides.	
$(CH_2)''$	......	245	Liquid.	311	Liquid.	371
$(C_2H_4)''$	Liquid.	274	Liquid.	344	Liquid.	398
$(C_3H_6)''$	Liquid.	311	Liquid.	371	222	422
$(C_4H_8)''$	Liquid.	344	Liquid.	398	241	446
$(C_5H_{10})''$	Liquid.	371	222	422	247	468

Normal alkides of Group VI. $X.(CH_2)_n.X.$

Relation 3. *The melting- and boiling-points of either the halogen or alkyl compounds of the hydrocarbon radicals of any one group increase as the atomic weight of the hydrocarbon radical increases.* (See Table III.)

Relation 4. *The differences between the boiling-points (and also between the melting-points) of the chlorides and bromides, bromides and iodides, chlorides and iodides (or between those of the methides and ethides, ethides and propides, propides and butides, &c.), increase algebraically from the first member of each series of hydrocarbon radicals up to the fourth or middle (tetrad)*

member and then diminish to the seventh or last member. (See Table IV.)

TABLE IV.—Illustrating Relations 4 and 5.

	Br—Cl.	I—Br.	I—Cl.	Et—Me.	Pr—Et.	Pr—Me.
Diff. in at. wts.	44·5	47	91·5	14	14	28
	B.P.	B.P.	B.P.	B.P.	B.P.	B.P.
C^{iv}	112	158	270	......	......	......
$(CH)^{iii}$	90	......	......	114	......	......
$(CH_2)^{ii}$	55	83	138	66	60	126
$(CH_3)^{i}$	28	39	66	......	29	......
$(C_3H)^{i}$	......	......	......	......	......	......
$(C_3H_2)^{ii}$	......	......	......	......	......	......
$(C_3H_3)^{iii}$	55	......	......	......	......	......
$(C_3H_4)^{iv}$	66	......	......	......	......	......
$(C_3H_5)^{iii}$	61	......	......	......	......	......
$(C_3H_6)^{ii}$	45	42	94	60	51	111
$(C_3H_7)^{i}$	24	29	53	37	33	70

The number of cases in which Relation 4 can be applied is unfortunately very limited ; but, in so far as it is applicable, the data obey exactly the same rule as those of the halogen and alkyl compounds of the elements.

RELATION 5. *The differences referred to in* (4) *increase as the difference between the atomic weights of the halogens (or of the alkyl radicals) increases. In the case where the difference between the alkyl radicals is the same, the differences between the boiling-points (or melting-points) diminish as the sum of the atomic weights of the several pairs of alkyl radicals increases.* (See Tables IV. and V.)

RELATION 6. *The differences referred to in* (4) *diminish algebraically as the atomic weight of the hydrocarbon radical increases.* (See Table V.)

Table V.—Illustrating Relations 5 and 6.

		Br—Cl.	I—Br.	I—Cl.	Et—Me.	Pr—Et.	Pr—Me.
	Diff. in at. wts.	} 44·5	47	91·5	14	14	28
		B.P.	B.P.	B.P.	B.P.	B.P.	B.P.
Normal halides and alkides of Group VII. $CH_3.(CH_2)_n.X.$	CH_3 ...	29	37	66	......	29 *	......
	C_2H_5 ...	27	33	60	29*	37	66 *
	C_3H_7 ...	25	31	56	37	33	70
	C_4H_9 ...	22	30	52	33	27	60
	C_5H_{11} ...	22	27	49	27	27	54
	C_6H_{13} ...	22	26	48	27	24	51
	C_7H_{15} ...	20	22	42	24	24	48
	C_8H_{17} ...	20	......	......	24	22	46
Normal halides and alkides of Group VI. $X.(CH_2)_n.X.$	$(CH_2)^{ii}$	55	83	138	66 *	61	124
	$(C_2H_4)^{ii}$	48	a. 60	a. 108	70	54	124
	$(C_3H_6)^{ii}$	45	49	94	60	51	111
	$(C_4H_8)^{ii}$	45	......	......	54	48	102
	$(C_5H_{10})^{ii}$	36	......	......	51	46	97
	$(C_6H_{12})^{ii}$	23	......	......	48	41	89

* These four exceptions are all due to the boiling-point of propane, C_3H_8, being taken too high. The number used is based on the data given by Lefebvre, who states that propane is condensed to a liquid at $-25°$ to $-30°$ C.

RELATION 7. (a) *The differences between the boiling-points (and also between the melting-points) of the halogen (or of the alkyl) compounds of the hydrocarbon radicals of each group diminish as we pass from the chlorides to the bromides, and thence to the iodides (or from the methides to the ethides, and thence to the propides, &c.).* (See Table VI.)

(b) *These differences also increase as the difference between the atomic weights of each pair of hydrocarbon radicals increases.* (See Table VI.)

In those cases where there is a common difference between the atomic weights of several pairs of hydrocarbon radicals, then the differences between the boiling-points increase as the sum of the atomic weights of the several pairs of hydrocarbon radicals diminishes. (See Table VI.)

TABLE VI.—Illustrating Relations 7 *a* & *b*.

Group VII. $CH_3.(CH_2)n.X$	X= Diff. in at. wts.	Chlorides. B.P.	Bromides. B.P.	Iodides. B.P.	Methides. B.P.	Ethides. B.P.	Propides. B.P.
$C_8H_{17} - C_7H_{15}$		24	24	20	24	24	21
$C_7H_{15} - C_6H_{13}$		26	24	20	27	24	24
$C_6H_{13} - C_5H_{11}$		26	26	25	27	27	24
$C_5H_{11} - C_4H_9$	$CH_2 =14$	29	29	26	33	27	27
$C_4H_9 - C_3H_7$		32	29	28	37	33	27
$C_3H_7 - C_2H_5$		34	32	30	29*	37	33
$C_2H_5 - CH_3$		36	34	30	...	29*	37
$C_8H_{17} - C_6H_{13}$		50	48	40	51	48	45
$C_7H_{15} - C_5H_{11}$		52	50	45	54	51	48
$C_6H_{13} - C_4H_9$	$2CH_2 =28$	55	55	51	60	54	51
$C_5H_{11} - C_3H_7$		61	58	54	70	60	54
$C_4H_9 - C_2H_5$		66	61	58	66*	70	60
$C_3H_7 - CH_3$		70	66	60	...	66*	70
$C_8H_{17} - C_5H_{11}$		76	74	65	78	75	70
$C_7H_{15} - C_4H_9$		81	79	71	87	78	75
$C_6H_{13} - C_3H_7$	$3CH_2 =42$	87	84	79	97	87	78
$C_5H_{11} - C_2H_5$		95	90	84	99	97	87
$C_4H_9 - CH_3$		102	95	88	...	99	97
$C_8H_{17} - C_4H_9$		105	103	91	111	102	97
$C_7H_{15} - C_3H_7$	$4CH_2 =56$	113	108	99	124	111	102
$C_6H_{13} - C_2H_5$		121	116	109	126	124	111
$C_5H_{11} - CH_3$		131	124	114	...	126	124
$C_8H_{17} - C_3H_7$		137	132	119	148	135	124
$C_7H_{15} - C_2H_5$	$5CH_2 =70$	147	140	129	153	148	135
$C_6H_{13} - CH_3$		157	150	139	...	153	148
$C_8H_{17} - C_2H_5$	$6CH_2 =84$	171	164	149	177	172	156
$C_7H_{15} - CH_3$		183	174	159	...	177	172
$C_8H_{17} - CH_3$	$7CH_2 =98$	207	198	179	...	201	193

* These exceptions are all due to the boiling-point of propane, C_3H_8, being too high; see footnote to Table V.

RELATION 8. *The differences between the boiling-points*[†] *of the halogen or of the alkyl compounds of the hydrocarbon radicals of the seventh group, and those of the hydrocarbon radicals of the other groups respectively, increase algebraically from the chlorides to the bromides, and thence to the iodides (or from the methides to the ethides, and thence to the propides, &c.).* (See Table VII.)

[†] Data are wanting as regards melting-points.

TABLE VII.—Illustrating Relations 8 and 9.

Group VI $X.(CH_2)n.X$ minus Group VII $CH_3.(CH_2)n.X$		X = Diff. in at. wts.	Chlorides. B.P.	Bromides. B.P.	Iodides. B.P.	Methides. B.P.	Ethides. B.P.	Propides. B.P.
CH_2	C_8H_{17}	-99	-141	-106	$b.-41$	-177	-135	-97
CH_2	C_7H_{15}	-85	-117	-82	-21	-153	-111	-75
C_2H_4	C_8H_{17}		-99	-71	......	-148	-102	-70
CH_2	C_6H_{13}	-71	-91	-58	-1	-126	-87	-51
C_2H_4	C_7H_{15}		-75	-47	......	-124	-78	-48
C_3H_6	C_8H_{17}		-64	-38	$b.+6\,d.$	-111	-75	-46
CH_2	C_5H_{11}	-57	-65	-32	$+24$	-99	-60	-27
C_2H_4	C_6H_{13}		-49	-23	......	-97	-54	-24
C_3H_6	C_7H_{15}		-39	-14	$+26\,d.$	-87	-51	-24
C_4H_8	C_8H_{17}		......	......	......	-78	-48	-22
CH_2	C_4H_9	-43	-36	-3	$+50$	$-66*$	-33	0
C_2H_4	C_5H_{11}		-23	$+3$	......	-70	-27	0
C_3H_6	C_6H_{13}		-13	$+10$	$+46\,d.$	-60	-27	0
C_4H_8	C_7H_{15}		......	......	......	-54	-24	0
C_5H_{10}	C_8H_{17}		......	......	......	-41	-24	0
CH_2	C_3H_7	-29	-4	$+26$	$+78$	$-29*$	0	$+28$
C_2H_4	C_4H_9		$+6$	$+32$	......	-37	0	$+27$
C_3H_6	C_5H_{11}		$+13$	$+36$	$+71\,d.$	-33	0	$+24$
C_4H_8	C_6H_{13}		......	......	......	-27	0	$+24$
C_5H_{10}	C_7H_{15}		......	......	......	-27	0	$+22$
CH_2	C_2H_5	-15	$+30$	$+58$	$+108$	0	$+37$	$+61$
C_2H_4	C_3H_7		$+38$	$+61$	......	0	$+33$	$+54$
C_3H_6	C_4H_9		$+42$	$+65$	$+97\,d.$	0	$+27$	$+51$
C_4H_8	C_5H_{11}		......	......	......	0	$+27$	$+48$
C_5H_{10}	C_6H_{13}		......	......	......	0	$+24$	$+46$
CH_2	CH_3	-1	$+66$	$+92$	$+138$	......	$+66*$	$+98$
C_2H_4	C_2H_5		$+72$	$+93$	......	$+29*$	$+70$	$+87$
C_3H_6	C_3H_7		$+74$	$+94$	$+125\,d.$	$+37$	$+60$	$+78$
C_4H_8	C_4H_9		......	......	......	$+33$	$+54$	$+75$
C_5H_{10}	C_5H_{11}		......	......	......	$+27$	$+51$	$+69$
C_2H_4	CH_3	$+13$	$+108$	$+127$	......	......	$+99$	$+124$
C_3H_6	C_2H_5		$+108$	$+126$	$+155\,d.$	$+66*$	$+97$	$+111$
C_4H_8	C_3H_7		......	......	......	$+70$	$+87$	$+102$
C_5H_{10}	C_4H_9		......	......	......	$+60$	$+78$	$+96$
C_3H_6	CH_3	$+27$	$+144$	$+160$	$+185\,d.$	......	$+126$	$+148$
C_4H_8	C_2H_5		......	......	......	$+99$	$+124$	$+135$
C_5H_{10}	C_3H_7		......	......	......	$+94$	$+111$	$+123$
C_4H_8	CH_3	$+41$	......	......	......	......	$+153$	$+172$
C_5H_{10}	C_2H_5		......	......	......	$+126$	$+148$	$+156$
C_5H_{10}	CH_3	$+55$	......	......	......	......	$+177$	$+193$

N.B. The numbers followed by a (d) are not strictly comparable with the others, as one of the substances is decomposed on boiling, so that its boiling-point cannot be determined with any degree of exactness.

The numbers marked with an * are exceptions to Relation 9. They are all due to the b.p. of propane, C_3H_8, being too high. *Cf.* footnote to Tables V. and VI.

RELATION 9. (a) *The differences referred to in Relation* 8 *increase algebraically as the algebraic difference between the atomic weights of the hydrocarbon radicals increases.* (See Table VII.)

(b) *In the case where several pairs of hydrocarbon radicals have a common difference in atomic weights, then the differences between the boiling-points of their halogen compounds increase as the sum of the atomic weights of the several pairs of hydrocarbon radicals increases.* This rule also holds for the alkyl compounds so long as the difference between the boiling-points is a minus quantity (*i. e.* so long as the boiling-point of the alkyl compound of the polyvalent hydrocarbon radical is lower than that of the corresponding alkyl compound of the monovalent hydrocarbon radical), but when this difference becomes a plus quantity the rule is reversed. (See Table VII.)

For the purpose of illustrating the above relationships we have chiefly made use of the compounds of the sixth and seventh groups of hydrocarbon radicals, because the sets of compounds belonging to these groups are much more complete than in the case of the other groups ; the rules, however, hold equally with the latter as with the former.

The above nine rules have been applied in 1997 cases, of which 71 (or 3·6 per cent.) are exceptions. The exceptions are distributed as follows :—

	HALOGEN COMPOUNDS.				ALKYL COMPOUNDS.			
	Melting-points.		Boiling-points.		Melting-points.		Boiling-points.	
	No. of cases.	No. of exceptions.	No. of cases.	No. of exceptions.	No. of cases.	No. of exceptions.	No. of cases.	No. of exceptions.
Relation I.	20	2	68	1	5	0	48	0
„ II.	20	0	60	1	8	0	49	0
„ III.	...	...	104	1	6	0	73	0
„ IV.	8	2	35	1	...	...	26	0
„ V.	1	0	66	0	...	...	30	1
„ VI.	...	...	78	1	...	...	42	6
„ VII. *a.* ...	...	...	100	0	...	...	73	7
„ VII. *b.* ...	...	...	103	0	2	0	102	14
„ VIII.	...	...	108	0	...	...	285	0
„ IX. *a* & *b.*	...	...	106	2	...	...	361	32
Total	49	4 =8°/₀	828	7 =0·8 °/₀	21	0	1089	60 =5·5 °/₀

Of the above 71 exceptions no less than

45 are due to the b.p. of propane, C_3H_8, being too high.
 5   "   "   isobutane, $CHMe_3$, being too low.
 2   "   m.p. of carbon tetrabromide, CBr_4, being
 —   too high.
 52

So that 52 of the 71 exceptions would be accounted for by errors in the boiling-points of two of the above compounds, and in the melting-point of the last one. As regards *propane* there is certainly a considerable error in its boiling-point, or rather in the number which has been assumed as the boiling-point in our investigations ; for its actual boiling-point has not been determined, the value used being in fact the mean temperature of condensation, viz. $-25°$ to $-30°$ (cf. footnote to Table V.). With respect to *isobutane*, the boiling-point employed was that $(-17°)$ given by Butlerow (*Annalen*, cxliv. 10). Konovaloff states that it boils below $-10°$ (*Bull. Soc. Chim.* (2) xxxiv. 333). Finally, *carbon tetrabromide* is not only an exception to some of the relations noted above, but it was also shown, in my paper on the Halogen Compounds of the Elements, that, owing to its abnormally high melting-point, it was the most marked exception to some of the rules there stated.

In conclusion it will be seen, by a comparison of this and my previous papers, that the above nine relationships, together with others of less importance, hold good for the following four classes of compounds :—

 (1) The Halogen compounds of the Elements (*i. e.* of elements with elements).
 (2) The Alkyl compounds of the Elements (*i. e.* of elements with hydrocarbon radicals).
 (3) The Halogen compounds of the Hydrocarbon Radicals (*i. e.* of elements with hydrocarbon radicals).
 (4) The Alkyl compounds of the Hydrocarbon Radicals (*i. e.* of hydrocarbon radicals with hydrocarbon radicals).

Though the periodicity of Relation 1 holds for all the four classes of compounds, yet the nature of the periodicity is not exactly the same *throughout* for the compounds of the hydrocarbon radicals as for those of the elements.

We are therefore justified in concluding that, with the exception just stated, the physical properties of the compounds of the hydrocarbon radicals (so far as investigated) follow the same rules and exhibit exactly the same relationships as the corresponding compounds of the elements.

In my next paper I hope to indicate the theoretical significance of this general fact.

Diagram of the Boiling-Points of the Normal Methides, Chlorides, and Bromides of the Hydrocarbon Radicals.

LXI. *Some Thermodynamical Relations.*—PART I.
By WILLIAM RAMSAY, *Ph.D., and* SYDNEY YOUNG, *D.Sc.* [*]

THE relations to be considered in the following pages are, we believe, well founded ; but we hope to confirm them by more exact experiments than have as yet been made.

It appears advisable here to state the share which each of the authors has had in this work. For our purpose, the equation

$$\frac{L}{s_1 - s_2} = \frac{dp}{dt} \cdot \frac{t}{J}$$

will be employed. The relations of the first term of this equation were the subject of a communication to the Chemical Section of the Philosophical Society of Glasgow in the year 1877 by Dr. Ramsay, which, however, he considered too incomplete to be published ; while the application of the last term of the equation to the vapour-pressures of substances, which formed the subject of a joint research by both authors, was independently discovered by Dr. Young. It is also right here to mention that some of the relations discovered by Dr. Ramsay have been pointed out subsequently and independently by Trouton (Phil. Mag. 1884, vol. xviii. p. 54).

The term $\dfrac{L}{s_1 - s_2}$ (where L represents the heat of vaporization of a liquid or solid substance at its boiling- or volatilizing-point, and where s_2 is the volume of the liquid or solid at these temperatures, and s_1 that of the gas into which one or other is converted), if stated in words, denotes the heat expressed in units required to produce unit increase of volume of substance at the temperature of ebullition of the liquid or volatilization of the solid.

Two laws have been discovered, representing certain relations between different liquids.

The first law may be stated thus :—*The amount of heat required to produce unit increase of volume in the passage from the liquid to the gaseous state at the boiling-point under normal pressure is approximately constant for all bodies;* or $\dfrac{L}{s_1 - s_2}$ = C.

The data on which this law is based are imperfect. The heats of vaporization of but few bodies have been determined

with accuracy; and we have recently shown in a communication to the Royal Society that the results obtained by Favre and Silbermann, by Regnault, and by Andrews for ethyl alcohol are only approximations to truth. It is probable that the data given for other substances less easy to obtain in a pure state are still less to be relied on. We have also shown in that paper that the density of saturated vapour of alcohol is normal, or nearly so, only at temperatures below 50°. Nevertheless, in calculating by means of the above-mentioned formula the constant for alcohol, it has been assumed that the saturated vapour of alcohol possesses normal density at 78°·4; and from want of knowledge it has similarly been assumed that at their boiling-points the saturated vapours of the other liquids to be considered have also normal density. It must therefore be acknowledged that considerable doubt rests on both the expressions in the term $\dfrac{L}{s_1 - s_2}$, and this doubt prevented the previous publication of these relations; but it will be seen in the sequel that the much more trustworthy determinations of vapour-pressures amply confirm the law which has been stated.

The following table exhibits these relations at normal pressure :—

Substance.	$s_1 - s_2$.	L.	$\dfrac{L}{s_1 - s_2}$.
Water	1695	537	0·3166
Methyl alcohol	865·9	263·7	0·3046
Ethyl alcohol...........	624·7	202·4	0·3240
Ethyl oxide	322·3*	90·5	0·2808
Methyl formate.........	417·1	117·1	0·2808
Methyl acetate	362·5	110·2	0·3040
Ethyl acetate...........	323·0	92·7	0·2870
Ethyl oxalate	256·2	72·7	0·2835
Amyl alcohol (?)	375·5	121·4	0·3238
Acetic acid..............	318·0†	101·9	0·3204
Benzene	370·6	92·3	0·2491
Bromine.................	169·2	45·6	0·2695
Phosphorus chloride..	209·5	51·4	0·2453
Carbon disulphide ...	343·3	86·7	0·2526
Methyl iodide	181·5	46·1	0·2539
Ethyl iodide	180·5	46·9	0·2598
Ethyl chloride	361·9	100·1	0·2767
Carbon tetrachloride .	186·3	46·9	0·2515
Chloroform	229·1	61·2	0·2673
Mercury.................	258·0	77·5	0·3004
Nitric peroxide	309·6‡	93·48	0·3019

* Determined by Horstmann, *Annalen*, 1868, Suppl. vi. p. 64.
† Determined by Ramsay and Young.
‡ Density taken as 39 (H=1) as an approximation.

It will be seen that these numbers vary between 0·2453 for phosphorus chloride and 0·3240 for ethyl alcohol. The alcohols, water, and acetic acid give all nearly 0·32; and benzene, and bodies containing halogens and sulphur give lower numbers, averaging 0·2564.

The sequel will show that these numbers cannot be regarded as experimental deviations from a constant; but that they have significance can hardly be denied. It would also appear that the nature of the element in the compound, and its amount influence the absolute value; though the nature and extent of this influence can hardly be formulated.

The second law is:—*If the amounts of heat required to produce unit increase of volume in the passage from the liquid to the gaseous state be compared at different pressures for any two bodies, then the ratio of the amount at the boiling-point under a pressure* p, *to the amount at another pressure* p_2, *is approximately constant for all liquids.*

Or, $\dfrac{L}{s_1 - s_2}$ at p_1, bears a constant proportion to $\dfrac{L}{s_1 - s_2}$ at p_2, for all liquids, and probably for all solids.

In support of this statement the facts to be adduced are as follows :—

Water.					Chloroform.			
P. mms.	T.	s_1-s_2. ccs.	L.	$\dfrac{L}{s_1-s_2}$.	T.	s_1-s_2 ccs.	L.	$\dfrac{L}{s_1-s_2}$.
300	76·4	4022	552·1	0·137	35·0	535	64·65	0·121
760	100·0	1695	536·5	0·317	61·0	229	61·2	0·267
1000	107·1	1313	531·5	0·405	69·3	178	60·4	0·339
2000	129·3	695	515·6	0·742	92·5	95·3	58·2	0·611
3000	143·3	479	505·7	1·055	108·5	66·3	56·6	0·854
4000	154·2	369	497·7	1·350	121·0	51·4	55·4	1·079
5000	162·8	301	491·6	1·633	131·0	42·1	54·5	1·294
6000	170·1	255	486·1	1·906	140·0	35·9	53·6	1·493
7000	177·0	222	481·3	2·168	148·0	31·4	52·8	1·684
8000	182·9	197	477·0	2·424	155·0	27·9	52·2	1·871

The ratios, placing $\dfrac{L}{s_1 - s_2}$ at 300 millims. pressure $= 1·0$ for each substance, are :—

P	300	760	1000	2000	3000	4000	5000	6000	7000	8000
Water	1·00	2·30	2·94	5·40	7·68	9·81	11·88	13·86	15·77	17·63
Chloroform...	1·00	2·22	2·81	5·06	7·07	8·94	10·72	12·38	13·96	15·51

Another method of comparison is to regard the value of $\dfrac{L}{s_1 - s_2}$ for water as equal to unity at each pressure, when the numbers for chloroform become

1·00 0·962 0·953 0·938 0·922 0·911 0·903 0·893 0·885 0·850.

Similar results may be obtained on comparing other bodies with water; it may be, however, remarked that the instance chosen is one of those in which least concordance is to be noticed. It is evident that here also the concordance is merely approximate.

Another point worthy of notice is this. The heat of vaporization is expended in at least two channels :—it produces expansion against pressure, thus doing external work; and it is partly expended in internal work on the molecules of the body. Now it follows from what has preceded that the internal and total work bear an approximately constant proportion to each other for any one pressure, whatever be the liquid. Thus at a pressure of approximately 760 millims. the ratio of external to total work is shown as follows :—

Substance.	Total work. / External work.	Substance.	Total work. / External work.
Bromine	11·09	Ethyl acetate	11·81
Phosphorus chloride	10·09	Ethyl oxalate	11·67
Carbon disulphide	10·39	Amyl alcohol	13·32
Methyl alcohol	12·53	Ethyl chloride	11·39
Ethyl alcohol	13·33	Benzene	10·25
*Ethyl oxide (ether)	11·55	Chloroform	10·99
Water	13·02	Carbon tetrachloride	10·35
Methyl iodide	10·45	Mercury	12·36
Ethyl iodide	10·69	*Nitric peroxide	12·42
Methyl formate	11·55	Acetic acid	13·18
Methyl acetate	12·51	Water	13·02

* Vapour-density found at a few degrees above boiling-point.

In the equation $\dfrac{L}{s_1 - s_2} = \dfrac{dp}{dt} \cdot \dfrac{t}{J}$, both terms are approximately known for a number of substances. But before comparing them it is necessary to reduce the pressures which have been given in the previous part of this paper in millimetres of mercury, to grams per square centimetre. The comparison has been made for water, with the following results :—

Pressures, in millim. of mercury.	$\dfrac{\mathrm{L}}{s_1 - s_2}$.	$\dfrac{dp}{dt} \cdot \dfrac{t}{\mathrm{J}}$.
300 . . .	0·137	0·1395
1000 . . .	0·405	0·414
2000 . . .	0·742	0·770
3000 . . .	1·055	1·110
5000 . . .	1·633	1·743

The non-equality of these numbers may be ascribed to various causes : want of accuracy in experiment, most probably in determination of the heats of vaporization, and the assumption that the density of the saturated vapour of water is normal at high pressures, are among the most likely. With such results for water, it was thought unnecessary to compare these terms for other liquids, where the constants are probably less accurately determined. These numbers, however, suffice to prove that the relations pointed out in the first part of this paper, although derived from observations and assumptions not always trustworthy, agree fairly well with those deduced from the vapour-pressures, which have been determined with a high degree of accuracy.

We now proceed to exhibit the relations between the vapour-pressures of various liquids. The constants of the bodies considered were determined by Regnault, Olszewski, Naumann, Isambert, Moitessier and Engel, and by ourselves.

If a curve be constructed to represent the relation of temperature to pressure for any substance, and if tangents be drawn to touch the curve at various points corresponding to certain temperatures, these tangents will give the rate of increase of pressure per unit rise of temperature ; in other words, the value $\dfrac{dp}{dt}$ for those temperatures.

If we construct curves for a number of substances, and determine the value of $\dfrac{dp}{dt}$ for each of them at the same temperature, it is clear that the values obtained will differ widely, and will be greater for volatile substances than for those which are less volatile. But if we determine the values of $\dfrac{dp}{dt}$ for the same series of bodies, not at the same temperature, but at the same pressure, the conditions under which the comparison is made will be more similar, and the resulting values may be expected to differ much less.

2 O 2

In the calculation of the vapour-pressures of a number of substances for each degree between certain limits of pressure, it became evident that at any given pressure the rate of increase was generally, though not always, greater for the volatile substances than for the less volatile.

It was found that the product of the absolute temperature into the rate of increase of pressure $\left(\dfrac{dp}{dt} \cdot t\right)$ at any given pressure was approximately the same for the bodies examined, but the differences were evidently too great to be ascribed to errors of experiment or of calculation. That this product should be approximately the same for different substances might perhaps be anticipated from the following considerations :—If there are two bodies, the absolute temperatures of which must be raised to 200° and 400° respectively, in order to produce a certain effect, the same for both, it might be expected that a further rise of temperature of 1° would produce a greater effect on the substance whose temperature was 200° than on that at 400°; for the rise of temperature in the first case is greater in proportion to the temperature to which the body has already attained than it is in the second, the rise in the one case being from 200° to 201°, and in the other from 400° to 401°. The rise of temperature would perhaps rather be proportional if the temperature of the hotter body were raised from 400° to 402°, or if the rise of temperature in each case were made proportional to the absolute temperature. In order, then, to make the conditions as similar as possible in the calculation of the value of $\dfrac{dp}{dt}$ for different substances, the magnitude of the unit degree of temperature should be made to vary in the same ratio as the absolute temperature of those substances, corresponding to the particular pressure at which they are compared ; or, in other words, keeping the unit degree constant, the value $\dfrac{dp}{dt}$ should be multiplied by the absolute temperature t.

The values of $\dfrac{dp}{dt} \cdot t$ were determined for a number of liquids at several different pressures ; and it was found that the products obtained for different stable substances at the same pressure were always approximately the same, whatever that pressure might be. Thus at a pressure of 400 millims. the following values were obtained :—

Carbon bisulphide . .	4436	1·000
Alcohol	5873	1·324
Chlorobenzene . . .	4724	1·065
Bromobenzene . . .	4703	1·060
Aniline	5124	1·155
Methyl salicylate . .	4959	1·112
Bromonaphthalene .	4930	1·111
Mercury	4812	1·085

This may be better seen by making one of these values equal to unity, and reducing the others in the same ratio. The second column is thus calculated.

Repeating this operation at another pressure, a second series of values was obtained; and these were reduced in the same way. It was at once noticed that the reduced numbers at the new pressure were identical within the limits of error of experiment and calculation with those at the first pressure.

The calculations were therefore continued so as to include the widest attainable ranges of pressure, and at every pressure the value of $\frac{dp}{dt} \cdot t$ for one substance was made equal to unity; and the others reduced in the same ratio. The values of $\frac{dp}{dt} \cdot t$ for water were made $= 1$, because the vapour-pressures of this substance have been determined by Regnault between wide limits of temperature with very great care; but it was noticed that the values for both water and alcohol were very much higher than for the other substances examined; and a similar comparison was therefore made by taking the values for carbon bisulphide as equal to unity.

It was then found that for pressures ranging between 150 and 1500 or 2000 millim. the reduced values for each substance, with the exception of mercury, were very nearly constant for all pressures.

In the case of alcohol and water, employing the vapour-pressures of water as determined by Regnault (*Mémoires de l'Académie*, vol. xxv.), and of alcohol as determined by Ramsay and Young, the ratio of the values $\frac{dp}{dt} \cdot t$ was seen to be the same at pressures between 150 and 20,000 millim.

Two methods of calculation were adopted. In the first and more accurate method the vapour-pressures for each degree were calculated by the method of differences; and from these

numbers the value of $\frac{dp}{dt}$ at any pressure could easily be calcu-
lated with very small error.   The time required by this pro-
cess is very great ; and it was only adopted in the case of
water, for which the pressures for each degree between $-32°$
and $230°$ have already been calculated (Balfour Stewart,
' Treatise on Heat '), and of carbon bisulphide, alcohol, chloro-
benzene, bromobenzene, aniline, methyl salicylate, bromonaph-
thalene, and mercury between certain limits of pressure,
generally 150 or 200 to 700 millim. (Ramsay and Young,
Chem. Soc. Journ. 1885, p. 640).

In all other cases tangents were drawn to touch the vapour-
pressure curves at points corresponding to definite pressures,
several curves being required for each substance on different
scales to admit of this being done.   With care, this method
yields fairly satisfactory results.

It has been mentioned that the identity of the reduced
numbers for any one substance holds at pressures ranging
between about 150 and 1500 to 2000 millim.   At lower pres-
sures it is much more difficult to determine the values of $\frac{dp}{dt}$
with accuracy, and the influence of experimental errors is
greater.   Moreover, it has been necessary provisionally to
adopt the method of tangents for all substances except water
and carbon bisulphide at low pressures ; and it is doubtful,
therefore, whether much confidence is to be placed in the
values at pressures below 150 millim.

As regards high pressures, with the exception of alcohol all
the substances have been investigated by Regnault ; and it may
be worth while to mention one or two facts which appear to
throw some little doubt on the accuracy of some of his determi-
nations at pressures above 2000 or 3000 millim.   In vol. xxvi.
of the *Mémoires de l'Académie* Regnault gives the vapour-
pressures of a large number of substances for each 5°, calcu-
lated from his empirical formulæ.   Many of these series have
been examined by the method of differences ; and it has been
found that in several cases the numbers forming the third set
of differences increase slowly up to pressures of from 2000 to
3000 millim., but decrease at higher pressures.   This is
notably the case with alcohol ; and it has been shown by
Ramsay and Young, in a paper read before the Royal Society
in May 1885, that the higher vapour-pressures of this sub-
stance as determined by Regnault are too low.   It has also
been pointed out by Vincent and Chappuis (*Compt. Rend.*
vol. c. p. 1216) that the vapour-pressures of methyl chloride

above 7 atmospheres are much higher than those calculated from Regnault's formula, the difference at 140° amounting to no less than 11·3 atmospheres.

Where this decrease is observable in the third set of differences, it seems therefore justifiable to doubt the accuracy of the results at the higher pressures.

It may be stated in conclusion:—(1) That the values of $\frac{dp}{dt}$. t are approximately the same for all stable substances at the same pressure, but that the differences are real, and are not due to errors of experiment or calculation ; and (2) that the rate of increase of this value $\frac{dp}{dt}$. t with rise of pressure is the same for all stable bodies, at any rate for pressures between 150 and 2000 millim., while for alcohol and water it is the same for all pressures between 150 and 20,000.

In the tables which follow, the values of $\frac{dp}{dt}$, t (absolute temperature), and $\frac{dp}{dt}$. t are given for a number of stable substances at definite pressures, also the reduced values of $\frac{dp}{dt}$. t, that for (1) water and (2) carbon bisulphide being made $= 1\cdot000$ at each pressure, the values for other substances at the same pressure being reduced in the same ratio.

The second series of tables contains similar data for several substances which dissociate more or less completely on their passage into the gaseous state. It will be seen that for such bodies the values of $\frac{dp}{dt}$. t at any pressure are considerably higher than for stable substances at the same pressure.

The initial letter of the name of the observer of the vapour-pressure of each substance is given in the table containing the values of $\frac{dp}{dt}$ at the foot of the vertical columns. R. stands for Regnault, R. and Y. for Ramsay and Young, O for Olszewski, N. for Naumann, I. for Isambert, M. & E. for Moitessier and Engel.

Absolute Temperatures (t) of various Stable Substances corresponding to Definite Vapour-pressures.

Pressure in millims.	C_2H_6OH Ethyl alcohol.	H_2O Water.	CH_3OH Methyl alcohol.	$C_6H_5NH_2$ Aniline.	$C_8H_8O_3$ Methyl salicylate.	$C_{10}H_7Br$ Bromo-naphthalene.	S Sulphur.	C_2H_4 Ethylene.	Hg Mercury.	$CHCl_3$ Chloroform.	C_6H_5Cl Chloro-benzene.	C_6H_5Br Bromo-benzene.	$C_4H_{10}O$ Ether.	CCl_4 Carbon tetrachloride.	C_2H_5Cl Ethyl chloride.	C_2H_5Br Ethyl bromide.	C_2H_5I Ethyl iodide.	CS_2 Carbon bisulphide.
10	269·25	284·3	259·0					123·0	450·0					281·0		250·0		
50	295·0	311·3	283·0					139·5	506·9					295·0		262·8		254·05
100	307·5	324·7	295·0	375·0	405·5			146·75	534·3			347·3	260·3	304·0	248·7	271·0	291·0	267·7
150	315·3	333·1	303·0	392·9	424·3			151·4	551·5		343·5	364·3	268·5	311·0	254·3	277·0	300·0	276·5
200	321·0	339·6	308·9	404·0	436·4	485·9	668·0	154·9	564·3	298·0	353·9	374·9	274·8	321·8	262·9	286·8	307·0	283·2
300	329·8	348·9	317·6	412·4	445·5	496·6	683·7	160·0	583·0	307·7	361·8	383·2	284·0	330·0	269·4	293·9	317·7	293·2
400	336·0	356·0	324·0	424·75	459·5	512·5	696·1	164·0	597·0	315·0	373·7	395·8	291·0	336·3	274·9	299·8	325·7	300·75
500	341·1	361·7	329·3	434·2	470·05	524·5	707·0		608·2	321·0	382·8	405·4	296·7	342·0	279·3	304·7	332·2	306·9
600	345·45	366·5	333·9	441·9	478·7	534·1	716·1		617·7	326·2	390·2	413·3	301·5	346·8	283·3	309·0		312·15
700	349·1	370·7	337·8	448·5	486·0	542·3	724·6		625·9	330·9	396·5	420·0	305·7	351·0	287·0	313·0		316·75
800	352·65	374·45	341·1	454·25	492·4	549·5	732·0		633·1	334·8	402·0	425·9	309·3	355·0	290·1	316·3		320·8
900	355·6	377·8	344·1	459·4	498·1	555·9	739·0		639·8	338·3		431·2	312·9	359·0	293·0	319·6		324·5
1000	358·4	380·85	346·1				763·0		645·4	341·7			316·0	373·9	305·0	332·8		328·0
1500	369·8	393·2	358·9				788·2		669·2	355·1			328·5	385·3	314·3	342·7		341·9
2000	378·0	402·5	367·1				820·8			365·5			338·0	403·1	328·5	358·0		352·3
3000	390·6	416·5	380·1							381·3			352·8	427·9	348·1	379·3		368·7
5000	408·3	435·85	398·1							404·2			373·4					391·7
10,000	435·7	465·65																
15,000	453·5	485·3																
20,000	467·1	500·5																

Values of $\dfrac{dp}{dt}$ for various Stable Substances at Definite Pressures.

Pressure in millims.	Ethyl alcohol C₂H₅OH	Water H₂O	Methyl alcohol CH₃OH	Aniline C₆H₅NH₂	Methyl salicylate C₈H₈O₃	Bromo-naphthalene C₁₀H₇Br	Sulphur S	Ethylene C₂H₄	Mercury Hg	Chloroform CHCl₃	Chloro-benzene C₆H₅Cl	Bromo-benzene C₆H₅Br	Ether C₄H₁₀O	Carbon tetrachloride CCl₄	Ethyl chloride C₂H₅Cl	Ethyl bromide C₂H₅Br	Ethyl iodide C₂H₅I	Carbon bisulphide CS₂
10	0·68	0·65	0·738	…	…	…	…	1·43	0·302	…	…	…	…	…	…	…	…	…
50	2·89	2·70	3·04	2·00	1·93	…	…	4·54	1·31	…	…	2·13	…	2·57	…	2·86	…	2·66
100	5·35	4·95	5·48	3·77	3·49	4·12	…	9·67	2·47	…	4·03	3·83	5·01	4·52	7·64	5·19	4·52	4·78
150	7·62	6·95	7·43	5·38	4·65	5·24	…	12·41	3·45	8·64	5·60	5·19	7·18	6·30	9·94	7·15	6·28	6·65
200	9·83	8·88	9·54	6·76	6·05	7·38	5·62	15·97	4·40	11·85	7·07	6·59	9·21	8·07	13·45	8·80	8·00	8·38
300	13·77	12·50	13·40	9·41	8·30	9·40	7·12	22·67	6·26	15·25	9·82	9·24	12·67	10·99	16·94	12·25	11·03	11·70
400	17·48	15·90	17·16	11·80	10·55	11·35	8·71	30·07	8·06	18·16	12·34	11·60	16·33	13·88	20·08	15·47	14·08	14·75
500	21·10	19·10	20·56	14·10	12·65	13·10	9·97	…	9·78	21·00	14·68	13·85	18·91	16·90	22·90	18·86	…	17·65
600	24·80	22·20	23·71	16·30	14·63	14·75	11·33	…	11·44	23·76	17·00	15·90	22·30	19·50	26·91	21·65	…	20·38
700	28·20	25·30	27·41	18·40	16·50	16·35	12·75	…	13·05	26·32	19·10	18·05	25·45	21·47	29·17	24·39	…	23·10
800	31·46	28·10	30·63	20·40	18·40	…	13·95	…	14·60	28·70	…	19·95	27·58	23·94	32·47	27·33	…	25·67
900	35·42	31·30	33·25	…	…	…	15·16	…	15·90	31·74	…	…	30·55	26·28	35·12	29·70	…	28·60
1000	38·58	34·00	36·68	…	…	…	…	…	17·65	…	…	…	33·27	28·33	…	32·45	…	30·80
1500	53·32	47·22	50·52	…	…	…	20·62	…	24·60	42·78	…	…	45·11	38·28	48·25	44·25	…	42·43
2000	66·61	59·80	65·39	…	…	…	26·27	…	…	52·98	…	…	58·54	48·75	60·90	55·00	…	52·40
3000	92·09	83·40	88·57	…	…	…	35·35	…	…	72·94	…	…	78·60	65·90	83·80	75·10	…	70·67
5000	138·28	125·00	134·24	…	…	…	…	…	…	104·70	…	…	116·00	96·62	119·80	108·9	…	105·00
10,000	238·40	215·30	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…
15,000	327·40	294·00	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…
20,000	408·40	365·00	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…
	R. (10 to 1000 mm.) and R. &Y. (above 1000 mm.)	R.	R.	R. &Y.	R. &Y.	R. &Y.	R.	O.	R.	R.	R. &Y.	R. &Y.	R.	R.	R.	R.	R.	R.

Values of $\frac{dp}{dt}\cdot t$ (where t is the absolute temperature) for various Stable Substances at Definite Pressures.

Pressure in mms.	Ethyl alcohol. C₂H₅OH.	Water. H₂O.	Methyl alcohol. CH₃OH.	Aniline. C₆H₅NH₂.	Methyl salicy-late. C₈H₈O₃.	Bromo-naphthalene. C₁₀H₇Br.	Sulphur. S.	Ethylene. C₂H₄.	Mercury. Hg.	Chloroform. CHCl₃.	Chlorobenzene. C₆H₅Cl.	Bromobenzene. C₆H₅Br.	Ether. C₄H₁₀O.	Carbon tetrachloride. CCl₄.	Ethyl chloride. C₂H₅Cl.	Ethyl bromide. C₂H₅Br.	Ethyl iodide. C₂H₅I.	Carbon bisulphide. CS₂.
10	183	184·8	191					176	136									
50	853	840·5	860	750	783			634	664			740		722		715		675·7
100	1642	1607	1617	1481	1481			1419	1320		1384	1395	1304	1333		1364	1315	1280
150	2403	2315	2251	2174	2029	2002	3754	1879	1903	2575	1982	1946	1928	1915	1900	1938	1884	1839
200	3155	3016	2947	2788	2695	2602	4868	2474	2483	3646	2558	2525	2531	2510	2528	2438	2456	2373
300	4541	4361	4256	4014	3814	3782	6063	3627	3650	4772	3670	3657	3598	3537	3536	3513	3504	3430
400	5873	5660	5560	5124	4959	4930	7049	4920	4812	5829	4724	4703	4752	4580	4564	4547	4586	4436
500	7197	6908	6770	6231	6056	6062	8113		5948	6850	5728	5724	5612	5684	5520	5654		5417
600	8567	8136	7917	7311	7110	7104	9239		7067	7862	6740	6678	6723	6669	6697	6597		6361
700	9845	9379	9259	8358	8125	8105	10210		8168	8812	7678	7688	7673	7446	7624	7537		7317
800	11094	10522	10448	9372	9165	9089	11203		9243	9709		8602	8530	8403	8372	8554		8235
900	12595	11825	11441						10173	10846			9559	9330	9420	9394		9281
1000	13827	12949	12585										10513	10170	10290	10371		10102
1500	19718	18567	18131				15733		13391	15191			14819	14470	14716	14726		14507
2000	25179	24070	24004				20706		16463	19364			19787	18783	19141	18848		18469
3000	35970	34736	33666				29015			27813			27730	26564	27528	26886		26056
5000	56460	54482	53440							42320			43314	41344	41702	41306		41128
10,000	103870	100250																
15,000	148480	142680																
20,000	190770	182680																

Reduced Values of $\frac{dp}{dt} \cdot t$, that for Water being made $=1\cdot000$ at each pressure, and the values for other substances at the same pressure reduced in the same ratio.

Pressure in millims.	Ethyl alcohol. C_2H_5OH.	Water. H_2O.	Methyl alcohol. CH_3OH.	Aniline. $C_6H_5NH_2$.	Methyl salicylate. $C_8H_8O_3$.	Bromo-naphthalene. $C_{10}H_7Br$.	Sulphur. S.	Ethylene. C_2H_4.	Mercury. Hg.	Chloroform. $CHCl_3$.	Chlorobenzene. C_6H_5Cl.	Bromobenzene. C_6H_5Br.	Ether. $C_4H_{10}O$.	Carbon tetrachloride. CCl_4.	Ethyl chloride. C_2H_5Cl.	Ethyl bromide. C_2H_5Br.	Ethyl iodide. C_2H_5I.	Carbon bisulphide. CS_2.
10	·991	1·000	1·034					·951	·736			·880		·859		·851		·804
50	1·014	,,	1·024	·892	·931			·754	·790			·868		·830		·849	·819	·796
100	1·022	,,	1·007	·922	·921			·863	·821		·861	·840	·811	·827	·821	·837	·814	·794
150	1·038	,,	·972	·939	·877	·865		·812	·822	·854	·856	·837	·833	·832	·838	·808	·814	·787
200	1·046	,,	·977	·924	·894	·863	·861	·820	·823	·836	·848	·839	·839	·811	·811	·806	·804	·787
300	1·041	,,	·976	·916	·874	·867	·860	·832	·837	·843	·842	·831	·825	·809	·806	·803	·810	·784
400	1·038	,,	·982	·905	·876	·871	·878	·869	·850	·844	·835	·829	·840	·823	·799	·818		·784
500	1·042	,,	·980	·902	·877	·877	·866		·861	·842	·829	·821	·812	·819	·823	·811		·782
600	1·053	,,	·973	·899	·874	·873	·865		·869	·838	·828	·820	·826	·794	·813	·804		·780
700	1·050	,,	·987	·891	·866	·864	·878		·871	·838	·819	·818	·818	·799	·796	·813		·783
800	1·054	,,	·993	·891	·871	·864	·864		·878	·821			·811	·789	·797	·794		·785
900	1·065	,,	·968				·865		·860	·838			·808	·785	·795	·801		·780
1000	1·062	,,	·972				·847		·880	·818			·812	·779	·793	·793		·781
1500	1·062	,,	·977				·860		·887	·805			·798	·780	·795	·785		·767
2000	1·046	,,	·997				·836			·801			·822	·765	·793	·774		·750
3000	1·036	,,	·969							·777			·798	·759	·765	·758		·755
5000	1·036	,,	·981										·795					
10,000	1·036	,,																
15,000	1·041	,,																
20,000	1·044	,,																

Reduced values of $\frac{dp}{dt}\cdot t$, that for Carbon-bisulphide being made $=1\cdot000$ at each pressure, and the values for other substances at the same pressure reduced in the same ratio.

Pressure in millims.	Carbon bisulphide CS_2	Ethyl iodide C_2H_5I	Ethyl bromide C_2H_5Br	Ethyl chloride C_2H_5Cl	Carbon tetrachloride CCl_4	Ether $C_4H_{10}O$	Bromo-benzene C_6H_5Br	Chloro-benzene C_6H_5Cl	Chloroform $CHCl_3$	Mercury Hg	Ethylene C_2H_4	Sulphur S	Bromo-naphthalene $C_{10}H_7Br$	Methyl salicylate $C_8H_8O_3$	Aniline $C_6H_5NH_2$	Methyl alcohol CH_3OH	Water H_2O	Ethyl alcohol C_2H_5OH
10	…	…	…	…	1·068	…	…	…	…	0·983	0·938	…	…	…	…	…	…	…
50	1·000	1·028	1·058	…	1·042	…	1·095	1·082	…	1·031	1·109	…	…	…	…	…	…	…
100	″	1·025	1·066	1·033	1·042	1·019	1·090	1·078	…	1·035	1·022	…	…	1·158	1·110	1·273	1·244	1·262
150	″	1·035	1·054	1·065	1·058	1·048	1·058	1·078	1·085	1·046	1·043	…	1·089	1·157	1·157	1·264	1·256	1·283
200	″	1·022	1·027	1·031	1·031	1·066	1·064	1·070	1·063	1·064	1·057	…	1·097	1·104	1·182	1·242	1·259	1·307
300	″	1·034	1·024	1·029	1·032	1·049	1·066	1·065	1·076	1·085	1·109	1·094	1·103	1·136	1·175	1·241	1·271	1·329
400	″	…	1·025	1·019	1·052	1·071	1·060	1·057	1·076	1·098	…	1·097	1·111	1·112	1·165	1·253	1·271	1·324
500	″	…	1·044	1·053	1·048	1·036	1·057	1·060	1·077	1·111	…	1·119	1·119	1·118	1·155	1·250	1·276	1·324
600	″	…	1·037	1·042	1·018	1·057	1·050	1·049	1·075	1·116	…	1·108	1·117	1·118	1·150	1·244	1·275	1·329
700	″	…	1·030	1·017	1·020	1·049	1·051	…	1·070	1·122	…	1·109	1·108	1·118	1·149	1·265	1·279	1·347
800	″	…	1·039	1·015	1·005	1·036	1·045	…	1·046	1·096	…	1·122	1·104	1·110	1·142	1·269	1·282	1·345
900	″	…	1·012	1·019	1·007	1·030	…	…	1·074	1·128	…	1·100	…	1·113	1·138	1·233	1·278	1·347
1000	″	…	1·027	1·014	0·997	1·041	…	…	1·047	1·135	…	1·109	…	…	…	1·246	1·274	1·357
1500	″	…	1·015	1·037	1·018	1·045	…	…	1·049	…	…	1·085	…	…	…	1·250	1·282	1·369
2000	″	…	1·021	1·057	1·020	1·072	…	…	1·067	…	…	1·122	…	…	…	1·300	1·280	1·359
3000	″	…	1·032	1·014	1·001	1·064	…	…	1·029	…	…	1·114	…	…	…	1·292	1·304	1·364
5000	″	…	1·004	…	…	1·053	…	…	…	…	…	…	…	…	…	1·299	1·333	1·380
10,000	″	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…	1·325	1·373
15,000	″	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…
20,000	″	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…

Values of $\dfrac{dp}{dt}$ for various Dissociable Substances at definite Pressures.

Pressure in millim.	Nitrogen peroxide. N_2O_4.	Ammonium chloride. NH_4Cl.	Ammonium carbamate. $CO_2N_2H_6$.	Chloral methyl-alcoholate. $CCl_3.CH \begin{cases} OH \\ OCH_3 \end{cases}$	Chloral ethyl-alcoholate. $CCl_3.CH \begin{cases} OH \\ OC_2H_5 \end{cases}$
10	...	...	0·99	......	......
50	...	1·91	3·75	2·97	2·94
100	5·2	3·63	7·02	5·46	5·47
150	8·1	4·98	10·13	8·26	7·91
200	11·3	6·26	12·71	10·23	10·17
300	15·6	8·39	18·57	14·33	14·08
400	20·47	10·74	23·48	19·30	18·06
500	24·27	13·25	...	......	22·34
600	...	15·70			
	R. and Y.	R. and Y.	N., I., and M and E.	R. and Y.	R. and Y.

Absolute Temperatures (t) of various Dissociable Substances corresponding to definite Vapour-pressures.

Pressure in millim.	Nitrogen peroxide. N_2O_4.	Ammonium chloride. NH_4Cl.	Ammonium carbamate. $CO_2N_2H_6$.	Chloral methyl-alcoholate. $CCl_3.CH \begin{cases} OH \\ OCH_3 \end{cases}$	Chloral ethyl-alcoholate. $CCl_3.CH \begin{cases} OH \\ OC_2H_5 \end{cases}$
10	...	...	270·9	......	......
50	...	524·7	289·9	331·2	334·0
100	256·0	542·8	299·4	343·3	346·1
150	263·1	554·6	305·1	350·8	353·7
200	268·1	563·3	309·8	356·1	358·1
300	275·9	577·3	316·1	364·2	367·4
400	281·4	587·9	321·0	370·3	373·8
500	285·9	596·0	...	......	378·7
600	...	603·0			

Products of $\dfrac{dp}{dt}$ into Absolute Temperatures $\left(\dfrac{dp}{dt} \cdot t\right)$ for various Dissociable Substances at definite Pressures.

Pressure in millim.	Nitrogen peroxide. N_2O_4.	Ammonium chloride. NH_4Cl.	Ammonium carbamate. $CO_2N_2H_6$.	Chloral methyl-alcoholate. $CCl_3.CH \begin{cases} OH \\ OCH_3 \end{cases}$	Chloral ethyl-alcoholate. $CCl_3.CH \begin{cases} OH \\ OC_2H_5 \end{cases}$
10	...	...	268	......	......
50	...	1002	1087	984	983
100	1331	1970	2102	1866	1893
150	2131	2762	3091	2898	2798
200	3030	3526	3938	3635	3642
300	4304	4844	5870	5219	5173
400	5787	6314	7537	7147	6751
500	6939	7897	...	......	8460
600	...	9467			

Reduced Values of $\left(\dfrac{ap}{dt} \cdot t\right)$; that for Water being made $=$ 1·000 at each pressure, and the values for other substances at the same pressure reduced in the same ratio.

Pressure in millim.	Nitrogen peroxide. N_2O_4.	Ammonium chloride. NH_4Cl.	Ammonium carbamate. $CO_2N_2H_6$.	Chloral methyl-alcoholate. $CCl_3.CH\left\{\begin{matrix} OH \\ OCH_3. \end{matrix}\right.$	Chloral ethyl-alcoholate. $CCl_3.CH\left\{\begin{matrix} OH \\ OC_2H_5 \end{matrix}\right.$
10	......	......	1·451	......	......
50	......	1·193	1·293	1·170	1·170
100	0·828	1·226	1·308	1·161	1·178
150	0·921	1·193	1·335	1·252	1·209
200	1·004	1·169	1·306	1·205	1·208
300	0·987	1·110	1·346	1·197	1·186
400	1·018	1·116	1·332	1·263	1·193
500	1·004	1·143	......	......	1·225
600	......	1·164			

Reduced Values of $\left(\dfrac{dp}{dt} \cdot t\right)$; that for Carbon-bisulphide being made $=1\cdot000$ at each pressure, and the values for other substances reduced in the same ratio.

Pressure in millim.	Nitrogen peroxide. N_2O_4.	Ammonium chloride. NH_4Cl.	Ammonium carbamate. $CO_2N_2H_6$.	Chloral methyl-alcoholate. $CCl_3.CH\left\{\begin{matrix} OH \\ OCH_3. \end{matrix}\right.$	Chloral ethyl-alcoholate. $CCl_3.CH\left\{\begin{matrix} OH. \\ OC_2H_5. \end{matrix}\right.$
10	...	...	...	......	......
50	...	1·483	1·609	1·456	1·456
100	1·043	1·540	1·643	1·458	1·480
150	1·159	1·502	1·681	1·576	1·522
200	1·277	1·486	1·659	1·532	1·535
300	1·255	1·412	1·711	1·521	1·508
400	1·298	1·423	1·699	1·611	1·522
500	1·281	1·458	...	......	1·562
600	...	1·488			

A relation may be observed between the two substances bromobenzene and chlorobenzene, and also between ethyl chloride, ethyl bromide, and ethyl iodide. The ratio of the absolute temperatures of the bodies in either group corresponding to any given vapour-pressure is a constant. Thus the ratio of the absolute temperature of bromobenzene to that of chlorobenzene when the vapour-pressure of both is 100 millim. $= \dfrac{364\cdot3}{343\cdot5}$, or 1·061; and at the other pressures up to 700 millim. the ratio remains absolutely constant at 1·059. The ratio of the absolute temperatures of ethyl bromide and ethyl chloride has been determined for pressures between 150

and 5000 millim., and the numbers found vary only between 1·089 and 1·091. The data for ethyl iodide are much less complete; the comparison with ethyl chloride can only be made at pressures between 150 and 500 millim., and with ethyl bromide between 50 and 500 millim. In the first case the ratio of the absolute temperatures varies between 1·206 and 1·209, and in the second case between 1·105 and 1·108.

<div align="center">[To be continued.]</div>

LXII. *On the Velocity with which Air rushes into a Vacuum, and on some Phenomena attending the Discharge of Atmospheres of Higher into Atmospheres of Lower Density. By* HENRY WILDE, *Esq.**

CONSIDERING the present condition of our knowledge respecting the mechanical properties of air and other gases, some apology might appear to be needed in bringing before this Society the results of an investigation touching some fundamental principles in pneumatics, which for more than a century have been considered to rest on foundations as secure as the laws of gravitation of the heavenly bodies. A survey of the history of the dynamics of elastic fluids will, however, show that, great as are the advances which have been made in this branch of science, the laws of the discharge of elastic fluids under the varied conditions of elasticity and volume are still left in much obscurity. The several circumstances which have combined to produce this anomalous state of our knowledge of this subject are :—(1) The application of the laws of discharge of inelastic fluids, without any modification, to those which are elastic ; (2) the confusion of the quantity of the discharge of elastic fluids after leaving the vessel, with the velocity of discharge through the aperture in the vessel ; and (3) the want of a sufficient number of experiments, under varied conditions and through sufficient range of pressure, to compare with the deductions derived from theory.

It has hitherto been assumed, as a leading proposition in pneumatics, that air rushes into a vacuum with the velocity which a heavy body would acquire by falling from the top of a homogeneous atmosphere of the same density as that on the earth's surface ; and since air is about 840 times lighter than water, if the whole pressure of the atmosphere be taken as equal to support 33 feet of water, we have the height of the homogeneous atmosphere equal to 27,720 feet, through which, by the free action of gravity, is generated a velocity of 1332

---

* Communicated by the Author, having been read at a Meeting of the Manchester Literary and Philosophical Society, October 20, 1885.

feet per second.   This, therefore, is the velocity with which air is considered to rush into a vacuum, and is taken as a standard number in pneumatics, as 16 and 32 are standard numbers in the general science of mechanics, expressing the action of gravity on the surface of the earth.

Now, so far as I am aware, no experiments have hitherto been made directly proving this important proposition.   It is true that attempts have been made to determine the initial velocity by discharging air at extremely low pressures into the atmosphere ; but, apart from the conditions of the discharge into the air and into a vacuum being different, the history of physical science shows that it is unphilosophic to predicate absolute uniformity of any law through the order of a whole range of phenomena of the same kind ; as nature is full of surprises when pushed to extremes, or when interrogated under new experimental conditions.

It was long ago shown by Faraday[*] that, in the passage of different gases through capillary tubes, an inversion of the velocities of different gases takes place under different pressures, those which traverse quickest when the pressure is high moving more slowly as it is diminished.   Thus, with equal high pressures, equal volumes of hydrogen gas and olefiant gas passed through the same tube in $57''$ and $135''\cdot5$ respectively ; but equal volumes of each passed through the same tube at equally low pressures in $8'\ 15''$ and $8'\ 11''$ respectively.   Again, while the velocities of discharge of inelastic fluids are as the square roots of the heads, some mathematicians have justly considered that this law does not apply to those which are elastic, and have assumed with good reason (though what appears unlikely at first sight) that the velocity of air discharged into a vacuum is the same for all pressures.   But whatever differences of opinion there may be amongst natural philosophers on this point, all are agreed in estimating the quantity of air discharged from a higher into air of a lower density, from the difference between the two densities, as in the similar case of the discharge of inelastic fluids, by the difference or effective head producing the pressure.   This mode of determining the amount of the discharge from a higher to a lower density, like that of the velocity of the atmosphere into a vacuum, has not, so far as I know, been made the subject of experiment through any considerable range of pressure.   It therefore appeared to me that, as each gas has its specific velocity of discharge, such a series of experiments might be useful in confirming and extending our knowledge of the dynamics of elastic fluids.   In the course of

[*] Quarterly Journal of Science, 1818, vol. vii. p. 106.

these experiments I have met with some results which I thought of sufficient importance to bring before the Society.

The apparatus employed in this investigation consisted of two strong cylinders of cast iron, shown in the engraving. The small cylinder, A, had an internal capacity of 573 cubic inches, while the large cylinder, B, had a capacity of 8459
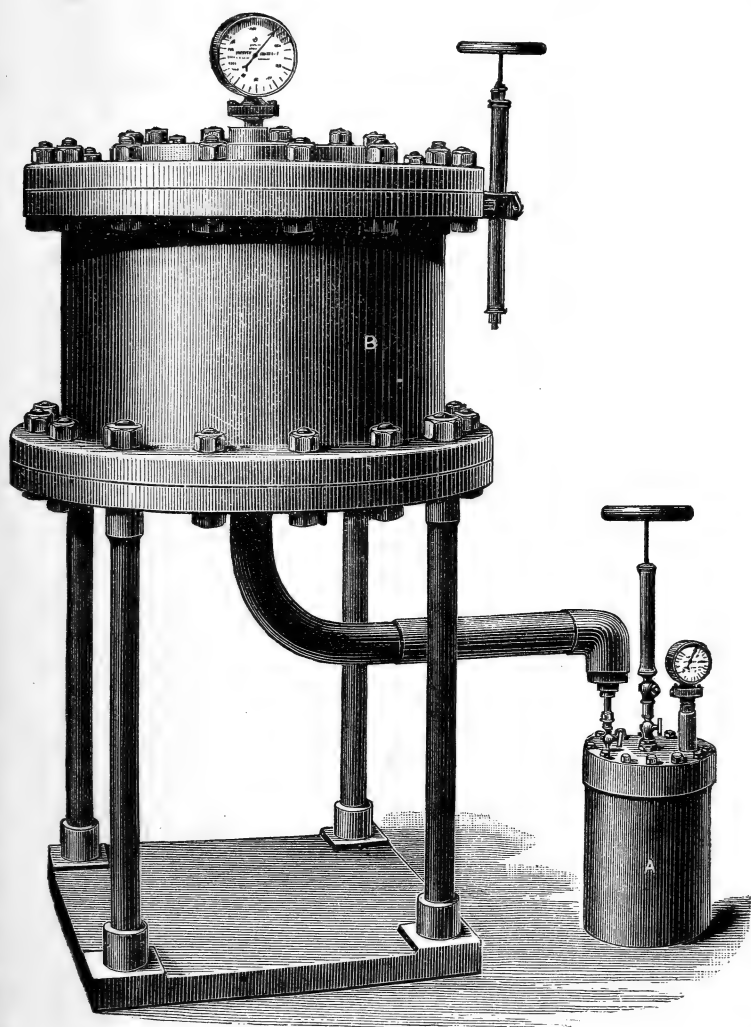
cubic inches, or about fifteen times the capacity of the cylinder A. To the top of this cylinder was fitted a syringe for

condensing the air up to nine atmospheres, and also a Bourdon's pressure-gauge of an improved construction, graduated through every pound of the above pressure. The accuracy of this gauge was tested in my presence by the constructors, Messrs. Budenberg and Co., through the whole range of pressure, by comparing its readings with a column of mercury of equivalent height. For pressures of 15 pounds above, and for pressures below the atmosphere, a mercurial gauge and a Bourdon's vacuum-gauge were employed, the readings of which were compared with each other : 30 inches of mercury were considered equal to one atmosphere, and 2 inches of mercury to one pound of pressure. The upper part of the glass tube of the mercurial gauge was fitted with a brass cap and screw-stopper, so that it could readily be used as a pressure-gauge, or as a vacuum-gauge when required. The discharging arrangement on the cylinder A consisted of a stopcock and union for securing a thin plate, through which the discharge was made. The orifice in the plate opened as required, either directly into the atmosphere or into the end of a short iron tube two and a half inches internal diameter, communicating with the bottom of the cylinder. The thin plate was a small disk of tinned iron, three quarters of an inch in diameter and one hundredth of an inch in thickness. The centre of the disk was pierced with a circular hole two hundredths of an inch in diameter. The size of the hole was accurately determined by means of a wire expressly drawn down to the above diameter ; the wire being calibred by one of Elliott's micrometer-gauges, divided into thousandths of an inch. The hole in the plate was enlarged so as to fit tightly the gauged wire, and the burrs on each side of the hole were carefully removed, as this small amount of projection, as Dr. Joule has shown*, exercises a notable influence on the rate of discharge through apertures in thin plates.

The general reasonings, and the inferences drawn from the experiments to be described, are based on Boyle and Mariotte's law of the density of a gas being as the pressure directly, and the volume as the pressure inversely for constant temperatures.

I have said that the capacity of the cylinder A was 573 cubic inches, which represents the same number of cubic inches of air in the vessel at atmospheric pressure of 15 lb. on the square inch ; and, generally, n times 573 cubic inches

---

* Memoirs of the Manchester Literary and Philosophical Society, vol. xxi. p. 104.

of air forced into the cylinder would be the equivalent of *n* atmospheres of absolute pressure.

In converse manner, 5 lb. of pressure, or one third of an atmosphere, is the equivalent of one third of 573 cubic inches, or the equivalent of 191 cubic inches of air at atmospheric pressure ; and, generally, 5 lb. of pressure is the equivalent of 191 cubic inches of air at atmospheric pressure and for all the higher pressures.   The mode of experiment was as follows:—Air was forced into the cylinder to the required density, and after the heat of compression had subsided, the time of each 5 lb. reduction of pressure was taken by means of a half-seconds pendulum, commencing its oscillations at the moment of discharge ; and the stopcock was suddenly closed, and the number of oscillations noted for every definite discharge and reduction of 5 lb. of pressure.   In my earlier experiments, it was found that when the air was compressed to nine atmospheres, and successive reductions of 5 lb. were made to the lowest pressure, the cooling of the air produced a notable effect in diminishing the rate of discharge.   By commencing the experiments with the lower pressures and increasing them by 10 lb. successively after each discharge of 5 lb., the changes of temperature atttending the changes of density of the air were kept within the limits of 5 lb. of pressure till the highest density was attained.   The small changes of pressure attending each discharge by the addition and abstraction of heat to and from the cylinder were after a little practice easily corrected, so that each discharge may well be considered as having been made under conditions of constant temperature. The large cylinder B was first used as a vacuum-chamber to receive the discharge from the small cylinder.   The chamber was fitted with an exhausting pump and suitable vacuum-gauges, and the pressure within the chamber was reduced to six tenths of an inch of mercury ; and that degree of vacuum was maintained during the experiments.

The following table shows the velocity of air flowing into a vacuum, as deduced from the time and difference of pressure for every 5 lb. from 135 lb. to 5 lb. absolute pressure.   The velocities of the first column are deduced from actual experiment, and in the next column the velocities are calculated from the difference of the area of the discharging orifice and the *vena contracta* by applying the hydraulic coefficient ·62.

TABLE I.—Discharge into a Vacuum 0·6 inch Mercury.
Barometer 29·42.   Thermometer 54° F.

Absolute pressure, in pounds per square inch.	Time of discharge, in seconds.	Velocity, in feet per second.	Velocity coefficient ·62.
135	7·5	750	1210
130	7·75	753	1214
125	8·0	759	1225
120	8·5	743	1198
115	9·0	734	1184
110	9·5	726	1171
105	10·0	724	1168
100	10·5	722	1165
95	11·0	725	1169
90	12·0	703	1134
85	13·0	688	1109
80	14·0	678	1094
75	15·0	675	1089
70	16·5	657	1060
65	18·0	650	1048
60	20·0	632	1020
55	22·0	628	1011
50	24·5	620	1000
45	27·0	624	1007
40	31·0	613	985
35	36·0	602	971
30	43·0	589	950
25	53·0	573	924
20	69·0	550	887
15	97·0	522	842
10	170·0	446	720

From this table it will be seen that the time of discharge of 5 lb. from 135 lb. absolute pressure is 7·5 seconds. Now, as 5 lb. pressure is the $\frac{1}{27}$ part of the total pressure, we have $\frac{573}{27} = 21\cdot22$ cubic inches of air from 135 lb. pressure discharged into the vacuum chamber in 7·5 seconds : or, in another form, since 5 lb. and 191 cubic inches of air at atmospheric pressure are equivalents, so 191 cubic inches condensed to 9 atmospheres $\frac{191}{9} = 21\cdot22$ cubic inches of discharge, as in the above calculation. Again, we have for a cubic inch extended into a cylinder 0·02 of an inch in diameter (the size of the discharging orifice), 265·25 feet × 21·22 = 5628 feet. Hence $V = \dfrac{5628 \text{ feet}}{7\cdot5 \text{ seconds}} = 750$ feet per second for the discharge of air from 135 lb. to 130 lb. into a vacuum through a hole in a thin plate. Or $V = \dfrac{750}{\cdot62} = 1210$ feet per second when the orifice is formed to the contracted vein. By the like method

of calculation the velocities for the discharge of each 5 lb. of pressure from 135 lb. to 10 lb. have been found.

The velocity with which air rushes into the vacuum, as seen from the table, is considerably less than that which has hitherto been assigned to it by theory, and is not constant for all pressures, as might have been expected from the known ratio of elasticity and density : the difference in the velocities between each discharge for the higher pressures, as will be seen, is so small as to be exceeded by experimental errors.   The amount of this difference will, however, appear more clearly when we are considering the velocity of air discharged into the atmosphere.   Meanwhile I may remark that the velocities increase with the pressures by small asymptotic quantities, so that the theoretic velocity of 1332 feet per second would be obtained at a pressure of 40 atmospheres if the law of Boyle and Mariotte held good for so high a density.

While the rate of each discharge may be considered approximately uniform for the higher pressures, the initial and terminal velocities of each discharge of 5 lb. for the lower pressures would be much different.   This is specially noticeable for the velocity (842 feet per second) assigned to atmospheric pressure of 15 lb. ; and as it was a matter of much interest that this important constant of nature should be determined with all the accuracy attainable, experiments were made to ascertain the velocity of discharge for every pound of pressure from 15 lb. to 2 lb.   In these experiments the readings were taken from the mercurial gauge, and the vacuum in the chamber was reduced to 0·4 of an inch of mercury.

The results obtained are shown in the table.

TABLE II.—Discharge into a Vacuum 0·4 inch Mercury.
Barometer 29·96.   Thermometer 60° F.

Absolute pressure, in pounds per square inch.	Time of discharge, in seconds.	Velocity, in feet per second.	Velocity-coefficient ·62.
15	16·0	633	1021
14	17·5	621	1001
13	19·0	614	990
12	21·0	606	977
11	23·0	600	968
10	25·5	596	961
9	28·5	593	956
8	32·5	584	942
7	37·5	577	931
6	45·0	563	908
5	55·0	559	901
4	70·0	542	874
3	102·0	497	802
2	180·0	421	679

By a calculation similar to that for the higher pressures, we obtain for the initial velocity with which the atmosphere rushes into a vacuum through a hole in a thin plate

$$V = \frac{573}{15} \times \frac{265\cdot25}{16} = 633 \text{ per second,}$$

or $V = \dfrac{633}{\cdot62} = 1021$ feet per second for the contracted vein.

That the differences between the theoretic and experimental velocities was not caused by the friction of the stream of air against the circumference of a smaller orifice being greater in proportion to that of the circumference of a larger orifice, was proved by discharging air of 15 lb. pressure through a hole one hundredth of an inch in diameter in another similar thin plate, when the times of discharge through the short range of 1 lb. of pressure were found to be in the ratio of 4 to 1, or inversely as the areas of the orifices.

Taking into further account the difference between the initial and terminal velocities due to the reduction of pressure from 15 lb. to 14 lb., the results of these experiments show that an absolute pressure of 30 inches of mercury, and at a temperature of 60° Fahrenheit, the atmosphere rushes into a vacuum with a velocity not greater than 1050 feet per second, or less than the velocity of sound.

Some anomalous rates of discharge which I obtained when air of different densities was discharged into the atmosphere, induced me to repeat the experiments with the same apparatus

TABLE III.—Discharge into the Atmosphere.
Barometer 30·17.　Thermometer 59° F.

Effective pressure, in pounds per square inch.	Time of discharge, in seconds.	Apparent velocity, per second.	Velocity-coefficient ·62.
15	8·0	1266	2043
14	8·25	1318	2126
13	8·5	1373	2214
12	9·0	1413	2280
11	9·5	1454	2345
10	10·0	1519	2450
9	10·5	1609	2595
8	11·5	1652	2664
7	12·5	1734	2797
6	13·5	1876	3026
5	15·5	1985	3202
4	17·5	2110	3403
3	22·0	2300	3710
2	29·0	2616	4219

and under precisely the same conditions as those which had been made into a vacuum as above described. The results are shown in Tables III. and IV.

On comparing the times of discharge in Table III. and the velocities calculated therefrom with the times and velocities in Table II., a remarkable difference will be observed in them for the same effective pressures. Thus, the velocity of discharge from 15 lb. to 14 lb. appears to be double that assigned to the same pressure when the discharge is made into a vacuum ; while in the discharge from 2 lb. to 1 lb. (the lowest pressure in the table) the velocity appears to be more than six times greater, or 4219 feet per second. No less remarkable than this apparent increase in the rate of discharge is the complete inversion of the order of the velocities as compared with those when the discharge was made into a vacuum for the same effective pressure. Now, we have knowledge of several causes competent to diminish the velocity of air of constant temperature flowing into the atmosphere, but none to increase the velocity except the form of the aperture, which in this case remained unchanged. Recognizing the fact that when air of 15 lb. effective pressure was discharged into the atmosphere the cylinder actually contained two atmospheres of absolute pressure, we are led to the conclusion that the phenomenal increase in the rate of discharge observed is caused by the external atmosphere acting as a vacuum, and offers no resistance to the discharge into it of air of 15 lb. pressure, which thereby becomes 30 lb. effective pressure. The velocity of air of 15 lb. effective pressure discharged into the atmosphere based on this conclusion is 1021 feet per second, the same as the velocity found for the discharge into a vacuum. For effective pressures below 15 lb. the velocities are compounded of the rate of discharge into a vacuum, and the resistance of the atmosphere without any regular ratio, but approximating to the square roots of the pressures.

That the atmosphere acts as a vacuum to the discharge of air into it of 15 lb. effective pressure, is further evident from the results obtained, and shown in Table IV.

Table IV.—Discharge into the Atmosphere.
Barometer 29·64.   Thermometer 58° F.

Effective pressure, in pounds per square inch.	Time of discharge, in seconds.	Apparent velocity, per second.	Velocity-coefficient ·62.
120	7·5	843	1360
115	7·75	852	1374
110	8·0	862	1390
105	8·5	852	1374
100	9·0	843	1360
95	9·5	842	1360
90	10·0	843	1360
85	10·5	851	1372
80	11·0	863	1392
75	12·0	844	1362
70	13·0	836	1348
65	14·0	833	1344
60	15·0	843	1360
55	16·5	837	1350
50	18·0	843	1360
45	20·0	843	1360
40	22·0	863	1392
35	24·5	886	1429
30	27·0	935	1509
25	31·0	980	1581
20	36·0	1053	1699
15	43·0	1178	1900
10	58·0	1311	2114

In this table it will be observed that the times of each discharge from 120 lb. to 15 lb. effective pressure into the atmosphere are identical with the times of discharge from 135 lb. to 30 lb. absolute pressure into a vacuum.   Hence we are able to formulate and prove the general proposition *that the atmosphere acts as a vacuum, and offers no resistance to the discharge of air of all pressures above two absolute atmospheres.*

Although the times of discharge for each reduction of 5 lb. of pressure, as we have seen, are the same as those for pressures one atmosphere higher, when the discharge was made into a vacuum, yet it seemed to me that a table showing the *apparent* velocities due to the effective pressure would be useful as exhibiting some further points of interest, and revealing the fallacy involved in estimating the velocities from the effective pressures.   On comparing the velocities of each discharge from 120 lb. to 40 lb., it will be seen that the theoretic velocity of 1332 feet per second is as nearly attained as the units of pressure and time adopted in these experiments

would permit. We have therefore in the table a measure of the difference of the theoretic and experimental velocities with which air rushes into a vacuum by the same method of calculation. This difference, as will be seen, amounts to exactly one atmosphere of pressure.

For each reduction of 5 lb. from 120 lb. to 40 lb. the times of discharge are inversely as the pressures ; and as the density of the issuing stream of air diminishes in the same proportion, the velocity of discharge is the same for all the pressures from 120 lb. to 40 lb., as shown in the table. Hence it appeared to me at the commencement of this investigation, that the theoretic and experimental velocities with which air rushes into a vacuum were rigorously exact. The anomalous and apparent increase in the velocities from 40 lb. to 10 lb., however, led me to suspect that the atmosphere in some manner affected the results, and induced me to make the discharge into a vacuum with the results shown in Table I.

That the phenomenal rate of discharge which I have described should not hitherto have manifested itself in some form, or be associated with some facts explanatory of it, would indeed be surprising considering the varied circumstances in which the discharge of elastic fluids comes into play. Hence, it has long been known that a jet of air issuing from an aperture in a vessel produces a rarefaction of the atmosphere near to the discharging orifice. This phenomenon was first observed on a large scale by Mr. Richard Roberts in the year 1824, and is described in a paper read before this Society in 1828*. Roberts noticed that when a valve was placed over an aperture in a pipe used for regulating a strong blast of air for blowing a furnace, the valve, instead of being blown off by the force of the blast, remained a short distance from the aperture, and required considerable force of the hand to remove it to a further distance. Subsequent experiments showed that the adhesion of the valve was caused by the partial vacuum formed between the valve and its seating by the expansion of the issuing air. These experiments were repeated and extended by Mr. Peter Ewart to similar effects produced by the discharge of steam through various apertures. Some of these experiments were described before this Society, and afterwards published in the Philosophical Magazine in 1829†. The degree of rarefaction produced by the discharge of air and high-pressure steam was carefully measured by

---

* Memoirs of the Literary and Philosophical Society, 2nd series, vol. v. p. 208.

† "Experiments and Observations on some of the Phenomena attending the Sudden Expansion of Compressed Elastic Fluids."

Ewart by means of gauges inserted in different parts of the jet. He also noticed the sudden fall of temperature from 292° to 189° F. in the rarefied part of the jet when steam of 58 lb. pressure was discharged into the atmosphere.

Sir William Armstrong also, in his experiments on Hydro-electricity in the year 1842[*], described a singular effect of a jet of steam by which a hollow globe made of thin brass, from two to three inches in diameter, remained suspended in a jet of high-pressure steam issuing from an orifice ; and when the ball was pulled on one side by means of a string, a very palpable force was found requisite to draw it out of the jet.

It is abundantly evident from these experiments, that whenever elastic fluids escape into the atmosphere a partial vacuum is formed near to the discharging orifice, the degree of vacuum depending on the density of the issuing stream. Ewart's ingenious explanation, that the vacuous space formed near the discharging orifice is caused by the joint action of elasticity and momentum of the suddenly released particles repelling each other beyond the distance necessary to produce equilibrium with the external pressure, has a high degree of probability ; but that this vacuous space should have the effect of increasing the rate of discharge could only be ascertained, as we have seen, by a direct comparison, under like conditions, with the amount of the discharge into a vacuum.

Having established the fact that the atmosphere acts as a vacuum to the discharge of air of all pressures above two atmospheres within the range of my experiments, it appeared to me that this phenomenon might only be a particular case of a general law of the discharge of elastic fluids, and that it would be interesting to know through what range of relative pressures in two vessels the one would act as a vacuum to the other. With this object air was compressed into the large receiving cylinder from two up to eight atmospheres absolute pressure, while air was condensed into a small discharging cylinder up to nine atmospheres of absolute pressure. The air was discharged from the same orifice as in the former experiments, and the time of discharge recorded for each atmosphere was for a reduction of 5 lb. of pressure. The results obtained are shown in the table.

[*] " On the Efficacy of Steam as a Means of producing Electricity, and on a Curious Action of a Jet of Steam upon a Ball," Phil. Mag. ser. 3. vol. xxii. p. 1.

TABLE V.

Absolute atmospheres.	0	1	2	3	4	5	6	7	8	
9	7·5	7·5	7·5	7·5	7·5	7·5	7·5	9·0	11·0	seconds.
8	8·5	8·5	8·5	8·5	8·5	8·5	10·0	13·5		,,
7	10·0	10·0	10·0	10·0	10·0	11·0	14·5			,,
6	12·0	12·0	12·0	12·0	12·5	16·0				,,
5	15·0	15·0	15·0	15·5	20·5					,,
4	20·0	20·0	20·0	25·5						,,
3	27·0	27·0	31·0							,,
2	43·0	43·0								,,
1	97·0									,,

In this table the first vertical column to the left shows the number of atmospheres in the small cylinder from which each discharge of 5 lb. was made into the receiver. The ordinal numbers at the head of the table indicate the atmospheres in the receiver when the discharge was made, commencing with vacuo ; and the time of each discharge, in seconds, is shown against the pressure in the discharging and receiving cylinders respectively. The times in the second and third vertical columns are obtained from those in Tables I. and IV., when the discharge was made into a vacuum and into the atmosphere. On examining these results, commencing with the lower pressures, it will be seen that for two atmospheres of absolute pressure, the time of discharge (43 seconds) was the same for a vacuum as it was when made into the atmosphere, as has already been demonstrated. It will also be seen that a pressure of two atmospheres in the receiver acts as a vacuum to four atmospheres in the discharging cylinder. This is evident from the equality of the time (20 seconds) when the discharge was made into one atmosphere or into a vacuum. The like ratio will also be observed up to three atmospheres in the receiver, which act as a vacuum to the discharge of six atmospheres of pressure from the small cylinder. As the pressure in the receiver was increased, the diminution of resistance of the recipient atmospheres becomes still more marked, till for the highest pressures we have the remarkable phenomenon of six atmospheres acting as a vacuum to the discharge of nine atmospheres of pressure. That this peculiar relation of the discharging and receiving atmospheres has not reached its full limit will be obvious from a comparison of the numbers in the table, from which it would appear that, for pressures exceeding those used in these experiments, the

resistance of the recipient atmospheres would be still further diminished correlatively with an increase in the amount of discharge.

With the object of giving more completeness to this research, experiments were made to ascertain through what range of relative densities the air in two vessels would act as a vacuum to the other for pressures below that of the atmosphere. The results are shown in Table VI., which are arranged in the same manner as those in Table V. The times in the second vertical column are taken from those shown in Table II. when the discharge was made into a vacuum for each pound of pressure, and the other times in the Table are those obtained for successive discharges into air of different densities below the atmosphere, the large cylinder being again used as a receiver.

TABLE VI.

Pounds per square inch.	0	1	2	4	6	8	10	12	14	
15	16·0	16·0	16·0	16·0	16·0	16·5	18·0	21·5	35·5	seconds.
14	17·5	17·5	17·5	17·5	17·5	18·5	20·5	26·5		,,
12	21·0	21·0	21·0	21·0	21·0	22·5	30·0			,,
10	25·5	25·5	25·5	25·5	26·5	33·5				,,
8	32·5	32·5	32·5	32·5	38·0					,,
6	45·0	45·0	45·0	47·5						,,
4	70·0	70·0	72·0							,,
2	180·0	190·0								,,

As equality in the times indicates equality in the quantities and velocities of the discharge for constant pressures, a simple inspection of the table shows that, for discharging pressures as low as 6 lb., the recipient air still acts as a vacuum up to half the density of the discharging stream, and the regularity of this law is maintained within the limits of 6 lb. and 90 lb. absolute pressure, as shown in Table V. For discharging pressures below 6 lb. the relative times of discharge and the resistance of the recipient air *increase*; and as we have already seen that the similar times and resistances for discharging pressures above six atmospheres *diminish*, the continuity of regular law is broken at both ends of the series of pressures, just as it is in the series of planetary distances and some other quantitative phenomena of nature.

LXIII. *Notices respecting New Books.*

Elementary Mechanics, including Hydrostatics and Pneumatics.
Revised Edition. By Oliver J. Lodge, *D.Sc. London, Professor*
of Experimental Physics in University College, Liverpool. London
and Edinburgh : W. and R. Chambers. 1885.

WHEN the first edition of this little book appeared, those who
knew the tendencies of the time in the teaching of Mechanics
were bold to predict for it a certain and speedy success. The call
for a new and revised edition is the evidence that these prophets
were right, and that the demand for sound, clear, elementary expo-
sition of the essential laws of matter and motion is a genuine and
growing one. Thomson, Tait, Maxwell, and Clifford took a fresh
look at the old and well-worn principles, and presented them to us
in a fashion that was implicitly full and complete as well as novel.
But their language is not that of the people—of the school-boy, of
the artizan-stud nt, of the young engineer ; and even the trained
mathematician finds that their terse statement does not reveal all
its meaning and all its bearing at the first glance. Maxwell's
' Matter and Motion ' is the best example : his booklet of text
would require a volume of commentary to develop its entire sig-
nificance ; and so while it gives practised readers all the delight of
severe healthful exercise, it is virtually sealed to the tyro. Some
work was wanted, then, which should lay open in ordinary language
what was hidden in the works of the masters. To do this without
sacrificing a jot of precision, without blurring by over- or under-
statement the sharp definition of the originals, without intruding
misleading illustrations intended to be vivid, without practising the
easy device of simplifying difficulties by evading them, itself requires
a kind of masterhood ; and this we think Professor Lodge to a
great extent in the first edition, to a greater extent in this second,
has come very near to indeed.

He has a happy audacity which in work of this kind is almost
genius : at any rate it gives the capacity of " taking a fresh look "
which talent often lacks, especially the talent of talented textbook-
writers. They have told us for generations that " force is that
which tends to produce motion," and that word " tends " covered
with its five letters a very chaos of doubts and difficulties to the
hapless beginner who thought. The word " force " was made more
mysterious by its definition. Lodge cuts the metaphysical knot,
and sends the student straight to the concrete by telling him that
" by the term *force* we are to understand muscular exertion, and
whatever else is capable of producing the same effects " (p. 13).
Again, after a brief and clear investigation of the normal accelera-
tion of a point moving in a circle, that intangible phantom to the
beginner, we are told—"Although the point is always *gaining* velo-
city normal to the curve or along its radius at this rate, it does not
follow that it ever *possesses* any such velocity. It is in fact impos-
sible for a point to possess any velocity except that along the curve

or at right angles to the radius of curvature; for as fast as velocity *along* the radius is generated, so fast does the direction of the radius change; in the same sort of way that a promise for to-morrow need never be fulfilled, because 'to-morrow never comes'" (p. 23). To give a puzzled student a hint like this is to "make his face to shine." Once more, in the part on Hydrostatics the question of the pressure on the base and sides of a vessel containing liquid is discussed without algebra or calculation, yet with perfect precision, and each of the student's difficulties is hit off and dissipated by a happy phrase or analogy: then, when by a kind of experimental induction he is led to see how all the cases are converging to a common principle, the last step is taken almost by the student himself—"in symbols, $P = sAh$. There is nothing more to explain. This simple formula contains it all" (p. 159). How much more truly *educative* is this method than the other that begins by raising a dust of symbols, and forces a reluctant consent for the bothered and unconvinced reader.

There is a further excellence in Professor Lodge's method which teachers will value. He every now and then reminds the student that there are large and interesting parts of the subject which are only touched on for the present; and not content with stating this, he gives him a glimpse of the directions in which these parts lie. He opens up vistas of future interest which encourage the student to persevere, in the hope that if he is faithful he will some day reach wider pastures. Thus at p. 50 enough is hinted to let the student guess "what Rigid Dynamics is about:" he is brought to the point where he must feel that some larger calculus is necessary. The mystery of gravitation is glanced at in pp. 15, 81, and glanced at in the right way, not as hopeless, but as stimulating. The Degradation of Energy is aptly illustrated at p. 84, and its Transformation at p. 86; a bit of Graphical Statics is worked in at p. 110, with a characteristic note that the bit is "an indication of quite a large art . . . . which may well occupy the student's attention at a later stage;" the measures of stability are touched on at p. 130, and meet halfway many perplexities of the inquiring student. Lastly, at p. 164, after finding the vertical fluid pressure on an immersed cube, we are told—"If we did not care for simplicity the same might be shown by the symbols for a solid of any irregular shape whatsoever, and a most important mathematical theorem it would be. You may make its acquaintance hereafter in a more general form under the name of Green's theorem."

This, we repeat, is something entirely different from the method of cramming a smattering of all things into a primer: no student can by such allusions as these to advanced matters have his head turned to the vain fancy that he knows all about them; one and all they come in as baits and lures to more earnest effort *now* and higher achievement *hereafter*.

We need say little here about the good and trustworthy apparatus of exercises abundantly provided, or the clearness and patness of the figures, or the terse Saxon of the writing. What we desire

most is to call the attention of enlightened teachers to a truly educative manual, which is no mere collection of dry bones, but alive with suggestion, and interest, and insight.

Transit Tables for 1886. *By* LATIMER CLARK, *F.R.A.S.*, *M.I.C.E.* London: Spon. (Pp. 71.)

These Tables constitute a *multum in parvo* for the use of those who do not care to turn over the pages of the bulky Nautical Almanac. Mr. Clark has added to the usefulness of his previous issues by appending the Right Ascensions of what he calls " Additional Stars," as well as the time of the Moon's southing on every alternate day of the year. He has also reverted to his original plan of giving the times of transit to hundredths of a second.

With the aid of this handy volume and one of the excellent Transit Instruments, invented by the Author, the merest amateur will be able to keep his clocks going in accordance with Greenwich or his own local time.

LXIV. *Intelligence and Miscellaneous Articles.*

VISIBLE REPRESENTATION OF THE FOCUS OF ULTRA-RED RAYS
BY PHOSPHORESCENCE. BY E. LOMMEL.

A WELL-KNOWN experiment for making the ultra-red rays visible is that of Tyndall. He uses a lens obtained by filling a spherical flask with a solution of iodine in bisulphide of carbon. This solution is opaque to the ordinary rays, but transmits the ultra-red rays and concentrates them in a focus ; the increased heating effect in this point is shown by the ignition of tinder or gun-cotton, or the incandescence of platinum.

This focus can easily be made visible by means of certain phosphorescent substances. Balmain's luminous paint is well adapted for the purpose ; or, still better, a greenish-blue phosphorescent calcium sulphide, the properties of which I have already described*. If this has been made slightly phosphorescent by ordinary daylight, it is increased to a bright luminosity by the less refrangible, and particularly by the ultra-red rays ; and when the radiation is moderately strong this lasts for hours, and even after the radiation ceases it gradually diminishes, but is visible for some time. After this cessation a dark spot appears on the irradiation place, because here, in consequence of increased emission, the luminous power is diminished or entirely destroyed.

If a transparent screen be made of this substance by spreading a layer of the powder between two glass plates cemented at the edges, the ultra-red region of the spectrum may be shown in greenish-blue phosphorescence near the red end of the spectrum, both on the front and back of the glass.

The same screen can be used to render visible the dark focus.

* Wiedemann's *Annalen*, vol. xx. p. 853.

If it be received on the screen, it appears as a bright spot on a feebly luminous ground, and changes after a lengthened action into a black spot, which has the same appearance as if a hole had been bored in a bright surface.

Instead of a solution of iodine or bisulphide of carbon, both which substances have their drawbacks, I use a solution of nigrosine in chloroform or alcohol. These solutions are quite black and only transmit ultra-red rays. Alcohol, it is true, strongly absorbs the ultra-red rays, so that the alcoholic solution only gives a focus of small thermal action. This fact is, however, advantageous for the above experiment; for the luminosity of the very sensitive phosphoescent substance lasts longer, and the blackening does not set in so rapidly, as if the focus were more intense. The far more diathermanous solution in chloroform gives a sufficiently hot focus for demonstrating the thermal action; nigrosine is insoluble in the still more diathermanous bisulphide of carbon.

With the great sensitiveness of phosphorescent substances for ultra-red rays, the flame of gas, of a lamp, or even a candle is sufficient to show the phenomenon. By means of the spherical flask, or, still better, by means of a lens with interposition of a plane parallel trough filled with the black liquid, a sharp *bright* (positive) image of the flame is received on the screen; after the radiation has ceased this lasts with continually decreasing intensity, and then turns into a *dark* (negative) image on a brighter ground. This is a kind of *photography by means of invisible ultra-red rays.*— Wiedemann's *Annalen*, No. 9, 1885.

ON THE TONES PRODUCED IN A PLATE OR A COLUMN BY FREQUENT DISCHARGES OF AN ELECTRICAL MACHINE. BY E. SEMMOLA.

The conductors of an induction machine are connected, by means of two wires 5 metres in length, with two binding-screws fixed at the opposite sides of a brass plate 1 millim. in thickness, which rests on an ebonite funnel. If, now, the path of the current is broken so that sparks strike across, the brass plate begins to sound. It sounds also even if a Geissler's tube or a lead wire is interposed in the break; and also if instead, a wire is led to earth from the one binding-screw, and in this a break is made. If the end of the broken wire is so far removed from the binding-screw that sparks pass, the tone is stronger, and can be distinctly discriminated from the sound of the sparks.

Even if the wires are connected with a metal plate which stands opposite that on the hearing-apparatus, sounds are heard in the last-mentioned experiments. If the plate on the hearing-tube is connected with the earth, the note is stronger. The same is also slightly the case when a glass plate is interposed. If the wire leading to earth is not broken, no sound is heard.

If the wires are connected with the insulated wire of a sonometer instead of with the brass plate, nothing is heard; if, however, an ebonite ear-trumpet is placed on the box the sound is audible.— *Beiblätter der Physik*, vol. ix. p. 671.

INDEX to VOL. XX.

END OF THE TWENTIETH VOLUME.

170° 165°

10° 10°

Mentschikoff

RALI

Namu

Odia

3000

2577

2768

2555

2925

5° 5°

2940

3440

3103

2905

2960

3080

3110

0 0

3020

3015

GROUP

2865

Canton

Enderbury 2900

2855
2370
1991

880
2835

Birnie

Phœnix

3000

Hull
335

Sydney

5° 5°

C

B A

UNION GROUP

1000 Nukuno

Fakaafo

10° 10°

2777

Swains 2746

2804 170°

Danger 955
1630 Atama

Nassau

A

CENTRAL PACIFIC

BATHYMETRIC MAP

1000 fath_____ 2000 fath........ 3000 fath ____

10°

5°

0

5°

10°

175°   180°   A   175°   170°

Ailck
Mentschikoff
Romanzoff
Erikub
Malcolab
Namu
Odia
Majuro
Arhoo
Jalu I.
Mili

RALICK CHAIN
RATACK CHAIN

Ebon

Taritari
Maraki
Tarawa
Maiana
Apamama
Nanouti
Tapuleouea   Peru   Byron
Onoaton
Ocean
Aroral

GILBERT   ISLANDS

Howland
Baker

Roef

McKeans

PHŒNIX GROUP

Canton
McCartaey 2903
2866
880   3370
2472   1991
Enderb
Phœnix

Gardner
Hull   Sydney
325
3111

3105
2906
2390

3080

3110

3020

3015

2865

1760

2333

2925

Tasuel
Hudson   Speldam
Depeyster
Ellice's
Nukulailai

ELLICE   ISLANDS

3305
1710

2300

3122
3080
3057
2606

UNION GROUP

Oatafu
Nukuono
Fakaafo

1770

Strathmore Shoal

Sophia

2336
2370
2050

3711

Swains   2746
2904

Danger 925
Suwarrow
Nassau

170°   175°   180°   175°   170°

Fig. 1

Fig 2.

Mintern Bros lith

Fig. 2.

Fig. 1.

Fig. 2.

Fig . 2 .

Sulphate of Zinc
S Z

Sulphate of Copper
S C

A

P

L

M

Q

B

Zn

Cu

Pure Zinc Rod

Electrotyped
Copper Rod.

Zinc Sulphate

Level of Contact
of
Liquids.

C

U

D

R

B
J
B'

P

1

a

R¹

b

P

12

Fig . 1 .

Fig . 2 .

Sulphate of Zinc
S Z

Sulphate of Copper
S C

Zn

Cu

Pure Zinc Rod

Electrotyped
Copper Rod.

Zinc Sulphate

Level of Contact
of
Liquids.

Fig . 3 .

Fig . 4 .

Fig . 5 .

Mintern Bros. lith .

Fig. 5.

9.

Fig. 10.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Fig. 9.

Fig. 10.

galvanometer

Γ G

α β

A

Coil   z

Coil

L_1 z   Coil

L_2

Q

Secondaries

M_1 Fig. 18. M_2

Coil   Coil δ

x   y

N_1 N_2

R   Primaries.   S

T

a

P   A   P   Fig. 19.

b α

Q

P   A β z   G   x + z δ

R   S

γ y

B

Fig. 11.

Fig. 16.

Fig. 17.

Fig. 18.

Fig 12

Fig. 13.

Fig. 19.

Fig. 14.

Fig. 15.

Mintern Bros. lith.

galvanometer

per broken curve shows the effect of
meter corrections, and was the curve
calculating the results of the
tions.

Curve A.

Curve B.

Curve C.

Curve D.

The upper broken curve shows the effect of thermometer corrections, and was the curve used in calculating the results of the observations.

Fig. 3.

Fig. 1.

Pump

e

Hg

f

d

a

c

Pump

Pump

g

b

b'

Gasometer

Hg

Fig. 2.

Hg

Fig. 1.

Fig. 2.

Curve of Den.^{y}

Max. Den.^{y}

Min.^{m} Den.^{y}

Fig. 3.

p.478.

Fig. 4.

Fig. 5.

A

C₁

Fig. 2.

m

d

Scale half full size.

A

b

Lamp

35 cms

s   d

m

c

g

w

p

Fig. 3.

Fig. 2.

Scale half full size.

Fig. 1.   Scale ¼ full size

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE,
AND
JOURNAL OF SCIENCE.

Being a Continuation of Tilloch's 'Philosophical Magazine,'
Nicholson's 'Journal,' and Thomson's 'Annals of Philosophy.'

FIFTH SERIES.

N° 122.—JULY 1885.

WITH THREE PLATES.

Illustrative of Prof. OLIVER LODGE's Paper on the Stream-Lines
of Moving Vortex-Rings.

Published the First Day of every Month.

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE,
AND
JOURNAL OF SCIENCE.

Being a Continuation of Tilloch's 'Philosophical Magazine,'
Nicholson's 'Journal,' and Thomson's 'Annals of Philosophy.'

CONDUCTED BY

SIR ROBERT KANE, LL.D. F.R.S. M.R.I.A. F.C.S.
SIR WILLIAM THOMSON, KNT. LL.D. F.R.S. &c.
AND
WILLIAM FRANCIS, PH.D. F.L.S. F.R.A.S. F.C.S.

FIFTH SERIES.

N° 123.—AUGUST 1885.

WITH THREE PLATES.

Illustrative of Dr. J. D. DANA's Paper on the Origin of Coral Reefs and
Islands, Dr. J. A. FLEMING's on the Use of Daniell's Cell as a
Standard of Electromotive Force, and Mr. J. BUCHANAN's on the
Thermoelectric Position of Carbon.

LONDON:

Double Number. Price Five Shillings.

NOTICE.

Owing to the length of several of the Communications with which we have been favoured, we have considered it desirable, in order to avoid delay in their publication, to issue a DOUBLE NUMBER this month instead of giving the usual *Supplementary Number* at the end of the Volume.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE,
22 ALBEMARLE STREET, LONDON, W.

The next ANNUAL GENERAL MEETING will be held at ABERDEEN, commencing on WEDNESDAY, September 9.

President-Elect,

The RIGHT HON. SIR LYON PLAYFAIR, K.C.B., M.P., Ph.D., LL.D., F.R.S.L. & E., F.C.S.

Notice to Contributors of Memoirs.—Authors are reminded that, under an arrangement dating from 1871, the acceptance of Memoirs, and the days on which they are to be read, are now, as far as possible, determined by Organizing Committees for the several Sections *before the beginning of the Meeting.* It has therefore become necessary, in order to give an opportunity to the Committees of doing justice to the several Communications, that each Author should prepare an Abstract of his Memoir, of a length suitable for insertion in the published Transactions of the Association, and the Council request that he will send it, together with the original Memoir, by book-post, on or before August 12, addressed thus:—" General Secretaries, British Association, 22 Albemarle Street, London, W. For Section.........." Authors who comply with this request, and whose Papers are accepted, will be furnished *before* the Meeting with printed copies of their Reports and Abstracts. If it should be inconvenient to the Author that his Paper should be read on any particular days, he is requested to send information thereof to the SECRETARIES in a separate note.

Reports on the Progress of Science, and of Researches intrusted to Individuals or Committees, must be forwarded to the Secretaries, for presentation to the Organizing Committees, accompanied by a statement whether the Author will be present at the Annual Meeting.

No Report, Paper, or Abstract can be inserted in the Report of the Association unless it is in the hands of the Secretary before the conclusion of the Meeting.

T. G. BONNEY, *Secretary.*

THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE,

AND

JOURNAL OF SCIENCE.

Being a Continuation of Tilloch's 'Philosophical Magazine,'
Nicholson's 'Journal,' and Thomson's 'Annals of Philosophy.'

FIFTH SERIES.

Nº 124.—SEPTEMBER 1885.

WITH TWO PLATES.

Illustrative of Dr. J. A. FLEMING's Paper on the Distribution of
Electric Currents in Networks of Conductors.

Now ready, medium 4to, price 1*s.*
PROBLEMS ON THE MOTIONS OF ATOMS.
By JOHN KINNERSLEY SMYTHIES,
Barrister-at-Law of the Inner Temple.

TAYLOR and FRANCIS, Red Lion Court, Fleet Street, E.C.

Seventh Edition. Price 2*s.* 6*d.*
HYGROMETRICAL TABLES
Adapted to the use of the Dry and Wet Bulb Thermometer.
By JAMES GLAISHER, F.R.S.

TAYLOR and FRANCIS, Red Lion Court, Fleet Street, E.C.

Royal 4to, cloth boards, price £1.
FACTOR TABLE FOR THE SIXTH MILLION,
CONTAINING THE
LEAST FACTOR OF EVERY NUMBER NOT DIVISIBLE BY 2, 3, or 5,
BETWEEN
5,000,000 and 6,000,000.
By JAMES GLAISHER, F.R.S.

Uniform with the above,
FACTOR TABLES FOR THE FOURTH AND FIFTH MILLIONS.
Price £1 each.

TAYLOR and FRANCIS, Red Lion Court, Fleet Street, E.C.

Demy 8vo, 98 pages and 2 Plates, price 2*s.* 6*d.* each, post free,
A limited number of Copies of Prof. OLIVER LODGE'S Memoir on
THE SEAT OF THE ELECTROMOTIVE FORCES IN THE VOLTAIC CELL,
Complete, with Appendix and Plates, can be obtained on application to
TAYLOR and FRANCIS, Red Lion Court, Fleet Street, E.C.

Demy 8vo, cloth, price £1, Volume I., with numerous Woodcuts, four Plates,
and Portrait.
THE SCIENTIFIC PAPERS
OF
J. P. JOULE, D.C.L., F.R.S.
Published by the Physical Society of London.
TAYLOR and FRANCIS, Red Lion Court, Fleet Street, E.C.

Demy 8vo, cloth, price 15*s.*, to Members of the Physical Society 10*s.*
THE SCIENTIFIC PAPERS OF
THE LATE
SIR CHARLES WHEATSTONE, D.C.L., F.R.S., &c.
Published by the Physical Society of London.
TAYLOR and FRANCIS, Red Lion Court, Fleet Street, E.C.

THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE,

AND

JOURNAL OF SCIENCE.

Being a Continuation of Tilloch's 'Philosophical Magazine,'
Nicholson's 'Journal,' and Thomson's 'Annals of Philosophy.'

CONDUCTED BY

SIR ROBERT KANE, LL.D. F.R.S. M.R.I.A. F.C.S.
SIR WILLIAM THOMSON, Knt. LL.D. F.R.S. &c.
AND
WILLIAM FRANCIS, Ph.D. F.L.S. F.R.A.S. F.C.S.

THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE,

AND

JOURNAL OF SCIENCE.

Being a Continuation of Tilloch's 'Philosophical Magazine,'
Nicholson's 'Journal,' and Thomson's 'Annals of Philosophy.'

FIFTH SERIES.

Nº 127.—DECEMBER 1885.

WITH TWO PLATES.

Illustrative of Prof. Osborne Reynolds's Paper on the Dilatancy of
Media composed of Rigid Particles in Contact, and Mr. T. Gray's on
Measurements of the Intensity of the Horizontal Component of the
Earth's Magnetic Field.

4155